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1976 ANNUAL SUMMARY REPORT

**AMES LABORATORY
USDOE**

**Iowa State University
Ames, Iowa**

MARCH 1978

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1976 ANNUAL SUMMARY REPORT

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FOREWORD

This report consists of collections of abstracts of papers published during the previous calendar year arranged in accordance with the project titles used in the USDOE Schedule 189 Budget Proposals. The collection of abstracts therefore supplements the listing of papers published in the Schedule 189.

Recent reports in this series are:

IS-1900	IS-2800
IS-2100	IS-3300
IS-2300	IS-3500
IS-2600	IS-3700
IS-3900	

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HIGH ENERGY PHYSICS

General Research and Development

PHYSICS RESEARCH

Experimental

DIRECT e^+e^- PAIR PRODUCTION BY 360 GeV/c π^- IN HYDROGEN

E. W. ANDERSON*, H. B. CRAWLEY, A. FIRESTONE, W. J. KERNAN, D. L. PARKER, B.-L. YOUNG, R. G. Glasser, D. G. Hill, M. Kazuno, G. McClellan, H. Price, B. Sechi-Zorn, G. A. Snow, F. Svrcek, B. Y. Oh, M. Pratap, G. Sionakides, G. A. Smith, J. Whitmore, N. N. Biswas, R. L. Bolduc, P. D. Higgins, J. M. Bishop, N. M. Cason, V. P. Kenney, D. S. Rhines, and W. D. Shephard
Phys. Rev. Lett. 37: 1593 (1976)

Abstract--We report on direct production of positron-electron pairs by 360-GeV/c pions incident on the Fermilab 30-in. hydrogen bubble chamber. These high-energy data are the first with liquid hydrogen, and are shown to be in agreement with quantum-electrodynamic calculations. For the region of four-momentum transfer considered, quantum electrodynamics predicts essentially equal contributions from production in the Coulomb field of the nucleus and the atomic electron.

EVIDENCE FOR LOCAL COMPENSATION OF TRANSVERSE MOMENTUM IN pp COLLISIONS AT 200 AND 300 GeV/c

D. Weingarten, E. W. ANDERSON, H. B. CRAWLEY, A. FIRESTONE, W. J. KERNAN, D. L. PARKER, B. Y. Oh, M. Pratap, G. Sionakides, G. A. Smith, J. Whitmore, D. G. Hill, M. Kazuno, G. McClellan, H. L. Price, B. Sechi-Zorn, G. A. Snow, F. Svrcek, R. J. Miller, J. J. Phelan, P. F. Schultz, L. Voyvodic and R. Walker
Phys. Rev. Lett. 37: 1717 (1976)

Abstract--Evidence is presented for local compensation of transverse momentum in pp collisions at 200 and 300 GeV/c. We compare the data with a model which contains no dynamical transverse-momentum correlations.

*Authors associated with Ames Laboratory are capitalized.

These data are used to determine a lower bound on the slope of the Pomeron trajectory.

OBSERVATION OF S^* PRODUCTION AT 1.98 GeV/c

M. BUTTRAM, H. B. CRAWLEY, D. W. DUKE, R. C. LAMB, R. J. LEEPER
and F. C. PETERSON

Phys. Rev. D 13: 1153 (1976)

Abstract--We have studied the S^* meson using data from the reactions $\pi^- p \rightarrow \pi^+ \pi^- n$ and $\pi^- p \rightarrow K^+ K^- n$ at 1980 MeV/c. The parameters of the S^* pole were found by fitting the dimeson mass spectra from these reactions to a Breit-Wigner resonance formula with a coherent background. The dimeson mass was calculated from the beam and neutron four-vectors, the latter being measured by a time-of-flight technique. The mass resolution is $\sigma = 4$ MeV/c². Dimeson production was identified by analyzing the final-state meson trajectories with a magnetostrictive wire spark-chamber spectrometer. The events in our data sample were required to have a slow forward-going neutron which restricted the allowed range of four-momentum transfers to $|t - t_{\min}| < 0.003$ (GeV/c)² in the S^* region. From a sample of 21700 $\pi^+ \pi^- n$ events and 52 $K^+ K^- n$ events, we find the position of the S^* pole to be $(970 \pm 5) - i(22 \pm 5)$ MeV/c² as compared to the present world average value of $(993 \pm 4) - i(20 \pm 4)$ MeV/c².

π^- p INTERACTIONS AT 360 GeV/c: MEASUREMENT OF THE TOTAL AND ELASTIC CROSS SECTIONS AND THE CHARGED-PARTICLE MULTIPLICITY DISTRIBUTION

A. FIRESTONE, E. W. ANDERSON, V. CHANG, H. B. CRAWLEY, W. J. KERNAN, D. L. PARKER, R. G. Glasser, D. G. Hill, M. Kazuno, G. McClellan, H. Price, B. Sechi-Zorn, G. A. Snow, F. Svrcek, B. Y. Oh, M. Pratap, G. Sionakides, G. A. Smith, J. Whitmore, N. N. Biswas, R. L. Bolduc, P. D. Higgins, J. M. Bishop, N. M. Cason, V. P. Kenney, D. S. Rhines and W. D. Shephard
Phys. Rev. D 14: 2902 (1976)

Abstract--In a sample of 108563 pictures taken with the Fermilab 30-inch hydrogen bubble chamber, exposed to a 360 GeV/c π^- beam, we have observed 19453 interactions in a selected fiducial region. The observed charged multiplicity distribution has been corrected for the effects of scan efficiency, errors in prong count, missed close-in vees, secondary interactions, and neutron stars and for Dalitz pairs. The two-prong events have been corrected for losses at low- t . The total cross section is measured to be 25.25 ± 0.35 mb, and the elastic cross section is 3.61 ± 0.11 mb with an exponential slope of $(8.82 \pm 0.30) (\text{GeV}/c)^{-2}$. The average charged-particle multiplicity for inelastic events is 8.73 ± 0.04 , and the second moment f_{-2} is measured to be 9.83 ± 0.23 .

SEARCH FOR PULSED GAMMA RAYS OF $\sim 10^{13}$ eV FROM NP 0532

R. A. ERICKSON, R. K. FICKLE, and R. C. LAMB
Astrophys. J. 210: 539 (1976)

Abstract--A ground-based Cerenkov light receiver located near Ames, Iowa, was aimed at the Crab Nebula during five nights of 1975 February and March to search for γ -ray emission from NP 0532. The time distribution of detected events shows no evidence for pulsation at either the main peak or interpulse phases. Data from one of the five nights show a statistically significant level of activity as determined by a χ^2 test, incompatible with events

random in time at less than the 1 percent level. This result and data from neighboring nights suggest the existence of a high-energy ($\geq 2 \times 10^{13}$ eV) flux, variable on a time scale less than a day, which is not at the main or interpulse phases. The pulsed photon intensity averaged over all five nights is:

$$I(\geq 2 \times 10^{13} \text{ eV}) = 1.2(+1.4, -0.9) \times 10^{-12} \text{ photons cm}^{-2} \text{ s}^{-1}.$$

SEMI-INCLUSIVE π^- CROSS SECTIONS IN pp INTERACTIONS UP TO 300 GeV/c

B. Y. Oh, M. Pratap, G. Sionakides, G. A. Smith, J. Whitmore, R. J. Miller, J. J. Phelan, P. F. Schultz, L. Voyvodic, R. J. Walker, E. W. ANDERSON, H. B. CRAWLEY, A. FIRESTONE, W. J. KERNAN, F. OGINO, D. L. PARKER, D. G. Hill, M. Kazuno, G. McClellan, H. L. Price, B. Sechi-Zorn, G. A. Snow and F. Svrcek
Nucl. Phys. B116: 13 (1976)

Abstract--Semi-inclusive π^- cross sections in 200 and 300 GeV/c pp interactions are presented and compared with lower energy data. In the target fragmentation region the data are compared to the hypothesis of semi-inclusive KNO scaling. The energy and charge multiplicity dependences of the semi-inclusive cross sections in the central region are studied and a simple parametrization of the semi-inclusive density function is described.

THREE AND HIGHER ORDER RAPIDITY DISTRIBUTIONS IN pp COLLISIONS AT 200 GeV/c

M. Pratap, B. Y. Oh, G. Sionakides, G. A. Smith, J. Whitmore, R. J. Miller, J. J. Phelan, P. F. Schultz, L. Voyvodic, R. Walker, E. W. ANDERSON, H. B. CRAWLEY, A. FIRESTONE, W. J. KERNAN, F. OGINO, D. L. PARKER, D. G. Hill, M. Kazuno, G. McClellan, H. L. Price, B. Sechi-Zorn, G. A. Snow and F. Svrcek
Nucl. Phys. B116: 1 (1976)

Abstract--Three-particle rapidity distributions have been studied for different charged multiplicities in pp interactions at 200 GeV/c. Appropriately defined semi-inclusive three-particle correlations are found to be sufficiently small, leading us to conclude that the three-particle density can be expressed

in terms of one- and two-particle densities. For events with more than four charged particles, a superposition approximation for the three-particle density holds surprisingly well. This approximation enables us to express all higher order rapidity distributions in terms of one- and two-particle distributions alone.

Theory

SIMPLE EXPLANATION OF THE UP-DOWN AMBIGUITY IN $\pi\pi$ AND $K\pi$ s-WAVE PHASE SHIFTS

N. W. DEAN and V. CHANG

Lett. Al Nuovo Cimento 16: 233 (1976)

Abstract--The "up-down" ambiguity in $\pi\pi$ and $K\pi$ scattering is shown to be a simple manifestation of the Gersten ambiguity, i.e. complex conjugation of the "Barrelet zero." Arguments are presented on this basis for choosing the "down" solution, independently of higher-energy data.

DIRECT e^+e^- PAIR PRODUCTION BY 360 GeV/c π^- IN HYDROGEN

E. W. ANDERSON, H. B. CRAWLEY, A. FIRESTONE, W. J. KERNAN, D. L. PARKER, B.-L. YOUNG, R. G. Glasser, D. G. Hill, M. Kazuno, G. McClellan, H. Price, B. Sechi-Zorn, G. A. Snow, F. Svrcek, B. Y. Oh, M. Pratap, G. Sionakides, G. A. Smith, J. Whitmore, N. N. Biswas, R. L. Bolduc, P. D. Higgins, J. M. Bishop, N. M. Cason, V. P. Kenney, D. S. Rhines and W. D. Shephard
Phys. Rev. Lett. 37: 1593 (1976)

For abstract see Experimental, page 1.

QUANTUM MEASUREMENT AND ALGEBRAIC QUANTUM FIELD THEORIES

B. DeFACIO

Foundations of Physics 6: 185 (1976)

Abstract--It is shown that the physics and semantics of quantum measurement provide a natural interpretation of the weak neighborhoods of the states on observable algebras without invoking any idea of "a reading error" or "a measured range." Then the state preparation process in quantum

measurement theory is shown to give the normal (or locally normal) states on the observable algebra. Some remarks are made concerning the physical implications of normal states for systems with an infinite number of degrees of freedom, including questions on open and closed algebraic theories.

BILINEAR QUANTUM FIELD THEORIES AND THEIR COHERENT STATES

B. DeFACIO and C. L. HAMMER

J. Math. Phys. 17: 267 (1976)

Abstract--The quantization method developed by Hammer and Tucker, which is based upon a set of equations of motion and their conserved currents rather than a canonical formalism, is extended to interacting systems. The operators of the theory are bilinear and are essentially self-adjoint on a dense domain which is spanned by a suitably chosen subset of the coherent states. Both proper and improper gauge transformations of the second kind are discussed. For the proper case, the connection is given between these transformations and coherent states, which are discussed in detail. One interesting result is that a "smeared" Fock space can be constructed for a system where the particles have the same average quantum numbers. For the improper case, the gauge transformation of the second kind is related to the purely absolutely continuous measure. The formalism is applied to two examples. One is a Dirac field minimally coupled to a massive vector field, and the other is Klauder's ultralocal models.

COMPOSITE STRUCTURE OF HADRONS AND WHY DATA LIE NEAR AN ISOSPIN BOUND

N. A. TÖRNQVIST

Phys. Rev. D 13: 1947 (1976)

Abstract--The remarkable fact that nondiffractive scattering data tend to lie dangerously close to an isospin bound is discussed and it is shown how

this phenomenon can be understood in models where the hadrons are composite. The isospin dependence is argued to be given by the interchange of low-momentum isospin-carrying constituents ("soft" quarks). The remaining constituents interact through strong ($I = 0$ gluon) forces which do not depend on isospin. Because of the small momentum carried by the interchanged constituents, the isospin dependence factorizes approximately into a real function (or matrix when spin effects are taken into account) which depends on $\underline{s}$ and $\underline{t}$. This function multiplies the isospin-independent gluon amplitude. There is a similarity between this factorization and the way in which radiative corrections, due to soft photons, factorize. In this framework saturation of an isospin bound can be understood as an approximate regularity of strong interactions.

HIGH-ENERGY BEHAVIOR OF FERMION-FERMION SCATTERING IN A SUPERSYMMETRIC FIELD THEORY

BING-LIN YOUNG, T. F. Wong and J. W. OPOIEN
Phys. Rev. D 14: 2687 (1976)

Abstract--The high-energy behavior of the fermion-fermion and fermion-antifermion scattering amplitudes of a class of field theories, containing a spin-1/2 fermion field, a scalar field, and a pseudoscalar field, are investigated. These theories consist of a supersymmetric model, the Yukawa model, and the linear σ model. In the leading-logarithm approximation, ladders with fermions running along the sides in the $\underline{t}$ channel and mesons as rungs dominate in each order of two classes of diagrams. The sums of the dominant series give rise to fixed Regge cuts for all the three theories; the amplitude of the supersymmetric theory possesses a definite signature, while those of the other two lack it. A comparison of the result of the supersymmetric

theory with the results of an asymptotically free theory and the spontaneously broken non-Abelian gauge theory is made.

PION DIFFRACTION DISSOCIATION INTO HEAVY MASS STATES

K. E. LASSILA and E. P. PIETILÄINEN

Particles and Fields-1976: Ed. R. Peierls (American Institute of Physics: New York, 1976)

Abstract--We study pion diffraction dissociation into the massive states $K\bar{K}^*$, $N\bar{N}$, and $Y\bar{Y}$. The Reggeized Deck model leads to predictions for the occurrence of threshold enhancements in the sub-energies of such states produced in πN collisions. Generally good agreement with available data is seen, with that for the $K\bar{K}^*$ being better than the data comparison for $N\bar{N}$ where the off-mass shell extrapolation distance is larger.

NUCLEAR PHYSICS

Nuclear Theory

GROUND STATE PROPERTIES OF MEDIUM-HEAVY NUCLEI WITH A REALISTIC INTERACTION

A. L. Goodman, J. P. VARY and R. A. Sorensen
Phys. Rev. C 13: 1674 (1976)

Abstract--The Brueckner $\underline{G}$ matrix appropriate for medium-heavy nuclei is obtained from the Reid soft-core nucleon-nucleon potential. The $\underline{G}$ matrix is strongly affected by the Pauli operator $\underline{Q}$, which is treated exactly (no angle averaging). Within the range of valence space energies $\underline{G}$ has a weak dependence on the starting energy ω . Ground state properties of deformed rare earth nuclei ($\underline{Z} = 64-76$, $\underline{N} = 90-102$) and spherical semimagic nuclei (Sn, Pb, $\underline{N} = 82$, $\underline{N} = 126$) have been calculated in the Hartree-Fock-Bogoliubov approximation with an inert core of 110 nucleons. Deformations and pair gaps are both determined by the $\underline{G}$ matrix. The systematic experimental dependence of $\epsilon_{\text{spherical}}$, β_2 , β_4 , Δ_p , Δ_n , and $\underline{E}_{\text{po}}$ (prolate-oblate energy difference) on $\underline{N}$ and $\underline{Z}$ is reproduced. However, the magnitudes of β_2 , Δ_n , and $\underline{E}_{\text{po}}$ are too small. This may be largely due to the lack of isospin dependence of the oscillator basis states. β_2 and $\underline{E}_{\text{po}}$ could receive additional significant contributions from core polarization of the 110 particle core which is neglected here. The Hartree-Fock-Bogoliubov ground states obtained with this realistic interaction provide a reasonable foundation for high spin calculations.

LOCALIZATION IN HEAVY-ION ELASTIC, INELASTIC, AND TRANSFER REACTIONS

P. J. Moffa, C. B. Dover, and J. P. VARY
Phys. Rev. C 13: 147 (1976)

Abstract--A quantitative technique for studying the localization of heavy-ion reactions in both coordinate ($\underline{r}$) and angular momentum ($\underline{L}$) space has been developed. A comparison of the degree of localization in elastic, inelastic, and one-particle transfer reactions is presented. For elastic scattering, the localization is studied as a function of the angular range of the data. A fully quantum mechanical relationship between $\underline{L}$ and $\underline{r}$ is demonstrated.

SEMIREALISTIC SHELL-MODEL INTERACTION FOR NEUTRON HOLE STATES IN ^{208}Pb

W. J. BALDRIDGE and J. P. VARY
Phys. Rev. C 14: 2246 (1976)

Abstract--The Brueckner $\underline{G}$ matrix from the Reid soft-core potential is taken for the leading contribution to the effective two-neutron hole interaction in the ^{208}Pb region. To accomodate the corrections expected from core polarization and other higher order effects, including truncation of the model space, we add phenomenological two-body pairing and multipole forces whose strengths are determined by fitting the ^{206}Pb spectrum. A satisfactory fit is obtained with an interaction where the average total contribution of the added terms is less than 45% of the interaction. The same total effective interaction is then shown to yield a satisfactory spectrum for ^{204}Pb which may indicate the neglected effective many-body forces are not important. A comparison with the results of McGrory and Kuo is presented to examine the impact on the effective interaction of limiting the model space. We conclude

the prospects are good for extending this approach to other nuclei below ^{208}Pb viewed as shell-model systems of valence holes in ^{208}Pb .

SURFACE-RESTRICTED EFFECTIVE INTERACTIONS IN A SHELL MODEL

APPLICATION TO ^{88}Sr

N. Auerbach and J. P. VARY

Phys. Rev. C 13: 1709 (1976)

Abstract--We compare conventional phenomenological effective interactions acting throughout the nuclear volume with some surface restricted effective interactions for the particle-hole spectrum and properties of ^{88}Sr in a basis of neutron and proton orbitals. The surface restricted forces produce greater configuration mixing and enhance the neutron particle-hole contributions to the lowest-lying states and thus result in better agreement with experiment.

COMMENT ON THE REDUCTION OF AN IMPORTANT 9-j SYMBOL

C. STASSIS and S. A. WILLIAMS

J. Math. Phys. 17: 480 (1976)

Abstract--An error in the formula for the reduction of an important 9-j symbol is pointed out, and the correct relationship is given.

EXACT SOLUTION OF THE QUADRUPOLE SURFACE VIBRATION HAMILTONIAN IN BODY-FIXED COORDINATES

T. M. CORRIGAN, F. J. MARGETAN, and S. A. WILLIAMS

Phys. Rev. C 14: 2279 (1976)

Abstract--Exact, closed-form eigenfunctions for the harmonic, quadrupole surface vibration model of Bohr are developed. These angular momentum labeled, multiplicity-resolved functions of β , γ , and the Euler angles are valid for an arbitrary number of phonons.

PARTICLE PERMUTATION SYMMETRY OF MULTISHELL STATES.

I. TWO SHELLS

S. A. WILLIAMS and D. L. PURSEY

J. Math. Phys. 17: 1383 (1976)

Abstract--A method is developed for constructing $\underline{N}$ -particle states of definite symmetry from $\underline{n}_1$ -particle and $\underline{n}_2$ -particle states of definite symmetry where $\underline{N} = \underline{n}_1 + \underline{n}_2$. A canonical resolution of the attendant multiplicity question is given. The results, which are a first step toward the construction of appropriate coefficients of fractional parentage, do not rely upon any particular form for the $\underline{N}$ -particle Hamiltonian. Rather, the results are based entirely upon properties of the symmetric groups $S_{\underline{n}_1}$, $S_{\underline{n}_2}$, and $S_{\underline{N}}$. The group theoretic problem which is the construction of irreducible representations of $S_{\underline{N}}$ from those of $S_{\underline{n}_1} \times S_{\underline{n}_2}$ is solved using induced representation theory together with projection operator techniques.

ON-LINE γ - γ ANGULAR CORRELATIONS OF TRANSITIONS IN ^{140}Ba

L. J. ALQUIST, W. C. SCHICK, JR., W. L. TALBERT, JR., and S. A. WILLIAMS

Phys. Rev. C 13: 1277 (1976)

Abstract--Angular-correlation measurements were made on 12 direct cascades and 5 skip cascades in ^{140}Ba . Levels in ^{140}Ba were populated from the 64-sec β decay of ^{140}Cs , which was populated from the decay of mass-separated ^{140}Xe . The most intense transitions were measured in coincidence with the first-excited state-to-ground-state transition in even-even ^{140}Ba . Definite spin assignments were made for eight levels and tentative spin assignments for five levels. Values are given for the angular-correlation coefficients, and multipolarity mixing ratios are listed where applicable. Systematics for $\underline{N}=84$ isotones are discussed in light of assignments made for ^{140}Ba .

BASIC ENERGY SCIENCES

Nuclear Sciences

NEUTRON AND FISSION RESEARCH

DECAY OF MASS-SEPARATED ^{138}I

W. R. WESTERN, JOHN C. HILL, W. C. SCHICK, JR., and W. L. TALBERT, JR.
Phys. Rev. C 14: 275 (1976)

Abstract--The γ rays following the β decay of mass-separated ^{138}I to levels in ^{138}Xe have been measured using Ge(Li) detectors for both singles and coincidence spectra. A level scheme of ^{138}Xe has been constructed in which eight transitions are placed between levels at 589, 1073, 1464, 1867, 1903, and 2398 keV. The implications of this study are discussed for the systematics of even-even Xe isotopes and $N = 84$ isotones.

^{200}Pt - ^{200}Au DECAY CHAIN

JOHN C. HILL, D. G. SHIRK, R. F. Petry and K. H. Wang
Phys. Rev. C 13: 2484 (1976)

Abstract--The γ decay of the ^{200}Pt - ^{200}Au decay chain to levels in ^{200}Au and ^{200}Hg was investigated using Ge(Li) detectors in singles and coincidence. Sources were produced by the $^{204}\text{Hg}(n, 2p3n)^{200}\text{Pt}$ and $^{198}\text{Pt}(t, p)^{200}\text{Pt}$ reactions. Thirty γ rays from ^{200}Au decay were placed in a level scheme involving 14 excited states in ^{200}Hg . γ transitions from the decay of ^{200}Pt were observed for the first time. Of 35 γ rays ascribed to the decay of ^{200}Pt , 31 were placed in a level scheme involving excited states of ^{200}Au at 60, 76, 104, 166, 240, 244, 293, 304, 390, and 469 keV. Limits on spin assignments for some of the new levels were determined.

DECAYS OF ^{88}Kr AND ^{88}Rb

R. L. BUNTING, W. L. TALBERT, JR., J. R. McCONNELL and R. A. Myer
Phys. Rev. C 13: 1577 (1976)

Abstract--The γ rays following the β decays of ^{88}Kr and ^{88}Rb have been studied, using both large volume Ge(Li) detectors for singles and coincidence measurements and anti-Compton spectrometry for singles measurements. Level schemes for ^{88}Rb and ^{88}Sr were constructed from the data and 74 of 81 γ rays observed in the decay of ^{88}Kr were placed in the ^{88}Rb level scheme with 23 excited states. For the decay of ^{88}Rb , all of the observed 27 γ rays have been placed in the (well known) level structure of ^{88}Sr . Spin and parity assignments have been deduced from β -decay $\log ft$ values and γ -ray transition patterns. Possible shell-model interpretations are presented for the level schemes.

GROUND-STATE β BRANCHING OF GASEOUS FISSION PRODUCTS AND THEIR DAUGHTERS FOR $A = 88-91$

F. K. WOHN, M. D. GLASCOCK, W. L. TALBERT, JR., S. T. Hsue and R. J. Hanson
Phys. Rev. C 13: 2492 (1976)

Abstract--The ground-state β branchings for several mass-separated Kr fission products and their daughters have been measured at the TRISTAN on-line separator facility at the Ames Laboratory Research Reactor. Absolute β counting was done with a 4π -geometry plastic scintillation detector and γ spectra were taken simultaneously with a Ge(Li) detector. The deduced values of the ground-state β branching β_{gs} , expressed as a percentage of decays, are: ^{88}Kr , 14 ± 4 ; ^{88}Rb , 78.0 ± 1.2 ; ^{89}Kr , 23 ± 4 ; ^{89}Rb , 25 ± 5 ; ^{90}Kr , 29 ± 4 ; ^{90}Rb , 37 ± 5 ; ^{91}Kr , 10 ± 4 ; ^{91}Rb , 5 ± 5 .

LEVEL SCHEMES OF ^{91}Rb AND ^{91}Sr POPULATED IN BETA DECAY

M. D. GLASCOCK, W. L. TALBERT, JR., and C. L. Duke

Phys. Rev. C 13: 1630 (1976)

Abstract--The decays of mass-separated ^{91}Kr and ^{91}Rb have been studied using γ -ray singles and coincidence techniques. From the decay of ^{91}Kr , a level scheme is proposed for ^{91}Rb consisting of 60 excited states and accomodating 218 of the 220 observed transitions. The half-life of the 108.8-keV level of ^{91}Rb has been determined to be 0.8 ± 0.3 nsec by delayed coincidence techniques. From the decay of ^{91}Rb , 109 of the 125 observed transitions are placed in a level scheme for ^{91}Sr containing 37 excited states. The half-life of the 93.6-keV level in ^{91}Sr has been measured to be 87.5 ± 3.0 nsec. Ground-state β branching has been determined to be $(10 \pm 4)\%$ and $(5 \pm 5)\%$ for the decays of ^{91}Kr and ^{91}Rb , respectively. Some spin-parity assignments are made, and a shell-model interpretation is suggested for some of the levels.

NUCLEAR DATA SHEETS FOR $A = 118$

G. H. CARLSON, W. L. TALBERT, JR., and S. Raman

Nucl. Data Sheets 17: 1 (1976)

Abstract--The 1960 version of the Nuclear Data Sheets for $A = 118$ has been revised on the basis of experimental data received before September 1973, with some later modifications. Experimental data concerning the nuclear structure of ten isotopes were compiled and used in the construction of the level schemes and J^π -assignments.

ON-LINE $\gamma\gamma$ ANGULAR CORRELATIONS OF TRANSITIONS IN ^{140}Ba
 L. J. ALQUIST, W. C. SCHICK, Jr., W. L. TALBERT, Jr., and
 S. A. WILLIAMS
 Phys. Rev. C 13: 1277 (1976)

For abstract see Nuclear Physics page 12.

TARGET DEVELOPMENTS AT TRISTAN
 W. L. TALBERT, Jr., F. K. WOHN, A. R. LANDIN, J. C. PACER,
 R. L. GILL, M. A. CULLISON, G. A. SHEPPARD, K. A. BURKE,
 K. L. MALABY and A. F. VOIGT
 Nucl. Instrum. Meth. 139: 257 (1976)

Abstract--Developments at TRISTAN to make available non-gaseous fission-product activities have progressed along three approaches: UF_4 samples to replace the traditional stearate sample, He-jet system connected to the separator ion source, and modification of the ion beam optics to allow placement of the ion source in the neutron beam. The status of each approach is presented in the light of the resulting availability of non-gaseous fission products of interest for systematic studies of nuclear structure of neutron-rich nuclei far from stability.

AN ISOTOPE SEPARATOR BEAM POSITION STABILIZER OF HIGH SENSITIVITY
 HAROLD D. SKANK
 Nucl. Instrum. Meth. 136: 73 (1976)

Abstract--A family of ion beam stabilizers in use on the TRISTAN isotope separator facility at the Ames Laboratory Research Reactor is described. The evolution of the concept is presented, a detailed discussion is given of a beam stabilizer for a magnetic β -ray spectrometer, and design variations appropriate for isotope separator high voltage power supply stabilization and beam switching magnet power supply stabilization are presented.

Materials Sciences

METALLURGY AND CERAMICS

Structure of Materials

SUPERCONDUCTIVITY IN SINGLET La-Pr AND IN NONMAGNETIC La-RARE EARTH ALLOYS

S. LEGVOLD, R. W. GREEN, B. J. BEAUDRY and J. E. OSTENSON
Solid State Comm. 18: 725 (1976)

Abstract--We show that concentration dependence of the superconducting transition temperature of d.h.c.p. LaPr alloys is almost identical to that of LaY and LaLu alloys. This suggests that Pr is in a singlet ground state and that life-time broadening caused by the 4f electrons of Pr have little effect on the superconducting process in LaPr. The depression of the transition temperature arises largely from pair weakening (or possibly crystal field effects) rather than pair breaking effects.

ELECTROTRANSPORT AND THERMOTRANSPORT OF OXYGEN AND NITROGEN IN VANADIUM METAL

J. Mathuni, O. N. CARLSON, E. Fromm and R. Kirchheim
Met. Trans. A 7A: 977 (1976)

Abstract--The effective valence of oxygen in vanadium was measured by a steady state electrotransport technique at six different temperatures in the range of 1500 to 2060 K. A temperature dependence in $\underline{Z}^*$ was observed decreasing from 1.51 at 1500 K to 1.15 at 2060 K.

In thermotransport experiments the heats of transport were measured for oxygen and nitrogen in vanadium as a function of solute concentration. Positive values of $\underline{Q}^*$ were obtained for both solutes at all concentrations

which, in view of their positive sign of $\underline{Z}^*$ in vanadium, is somewhat anomalous. The heat of transport of oxygen increases from 4.6 kcal/mole at 0.25 at. pct oxygen to 7.6 kcal/mole at 2.0 at. pct oxygen and above. Nitrogen shows a similar trend.

COMMENT ON DE HAAS-VAN ALPHEN MEASUREMENTS IN GADOLINIUM

J. E. Schirber, F. A. SCHMIDT, B. N. HARMON and D. D. Koelling
Phys. Rev. Lett. 36: 448 (1976)

Abstract--Fermi-surface cross sections for field along principal symmetry directions for Gd are presented which are in serious disagreement with those of previous investigators. This disagreement stems from the use of an incorrect value for the saturation magnetization. The new frequency values are compared with the results of a relativistic augmented-plane-wave band calculation.

ELECTROTRANSPORT OF CARBON IN MOLYBDENUM AND URANIUM

F. A. SCHMIDT and O. N. CARLSON
Met. Trans. A 7A: 127 (1976)

Abstract--The electrotransport velocity of carbon in molybdenum and uranium was measured over a temperature range slightly below their melting points. Carbon was found to have a positive effective valence of 2.26 to 1.74 in molybdenum over the temperature range of 1890 to 2320°C and a negative value of -5.0 in γ -uranium between 850 and 1000°C. The effective valences of nitrogen and oxygen were also observed to be positive in molybdenum and negative in uranium but their magnitudes were not determined. The diffusion coefficients for carbon in both metals were determined over the same temperature ranges. ¹⁴C was used as a tracer in the molybdenum work. The diffusion coefficient for carbon in molybdenum is described by the equation

$\underline{D} = \underline{D}_0 \exp(-\Delta H/RT)$ where $\underline{D}_0$ and ΔH are $0.033 \text{ cm}^2/\text{s}$ and 153 kJ/mole (36.60 kcal/mole), respectively. The values for $\underline{D}_0$ and ΔH for carbon in γ -uranium were determined as $0.218 \text{ cm}^2/\text{s}$ and 123 kJ/mole (29.40 kcal/mole), respectively. Electrotransport was shown to be an effective method of purifying a small amount of each metal with regard to carbon as indicated by resistance ratio measurements and chemical analysis. A correlation is also presented showing the relationship between the atomic size of the solvent metal and the sign of the effective charge of the migrating solute.

ELECTROTRANSPORT OF CARBON, NITROGEN AND OXYGEN IN SCANDIUM

F. A. SCHMIDT and O. N. CARLSON

J. Less-Common Metals 50: 237 (1976)

Abstract--The electrotransport behavior of carbon, nitrogen and oxygen in scandium was measured in both its α (h.c.p.) and β (b.c.c.) crystalline forms. Measurements made over the temperature range $1215\text{--}1440^\circ\text{C}$ showed that all three solutes migrate in the direction of the electron flow. Values for the mobility, diffusivity and effective valence were determined for each solute at four different temperatures. Highest mobilities were observed in the β form. In separate experiments iron and nickel were also observed to migrate toward the anode. Electrotransport was used to prepare a small amount of very pure scandium having a resistance ratio ($R_{300 \text{ K}}/R_{4.2 \text{ K}}$) of 520.

SINGLE CRYSTAL RESISTIVITY OF ERBIUM AND Er-Lu ALLOYS BETWEEN 2 AND 300 K

F. H. SPEDDING, B. J. BEAUDRY and W. D. CRESS

Rev. Chim. minérale 13: 62 (1976)

Abstract--The resistivity was measured along the $\underline{a}$ - and $\underline{c}$ -axes. A Néel temperature of 87, 68, 49 and 29 K was determined for Er, $\text{Er}_{0.75}\text{Lu}_{0.25}$

$\text{Er}_{0.50}\text{Lu}_{0.50}$ and $\text{Er}_{0.25}\text{Lu}_{0.75}$, respectively from the abrupt increase in resistivity along the c -axis with decreasing temperature. The experimental data are listed for temperatures at and below the Néel point. The experimental points in the paramagnetic range were fitted to an empirical equation of the type $\rho = A + BT + CT^2 + DT^{-1}$ by a least squares treatment. The constants for these equations which reproduce the experimental points within the accuracy of the experiment are given.

MAGNETIC MOMENTS OF FERROMAGNETIC GADOLINIUM ALLOYS

H. W. White, R. J. BEAUDRY, P. BURCARDT, G. LEEVOLD and B. N. HARMON

Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 329-330

For abstract see Magnetic Properties of Solids, page 45.

ELECTROTRANSPORT OF SOLUTES IN RARE EARTH METALS

O. N. CARLSON and F. A. SCHMIDT

Proceedings of the 12th Rare Earth Research Conference, ed., C. E. Lundin (Denver, Colorado: University of Denver and Denver Research Institute, 1976) Vol. I, pp. 460-469

Abstract--There has been considerable activity in recent years on electrotransport behavior of solute atoms in the rare earth metals. This effort appears to be derived from interest in serving two main objectives, (a) a better understanding of the transport behavior of solutes in metals and (b) the need for high purity rare earth metals. The common interstitial impurities, and many metallic impurities, exhibit high electrotransport velocities in the metals of this group. Thus, electrotransport offers promise of being an effective technique for ultra purifying the rare earths not only with respect to oxygen, carbon, and nitrogen, but also for iron, silicon and copper. This paper is a review of all the work, past and present, on electrotransport in rare earths and will be limited to transport in solid metals.

LIGHT SENSOR FOR ULTRAHIGH VACUUM SYSTEMS UTILIZING A SILICON PHOTOVOLTAIC CELL

B. K. LUNDE and F. A. SCHMIDT

Appl. Optics 15: 2625 (1976)

Abstract--A light sensor suitable for use as a pyrometer is described for application in an ultrahigh vacuum system. The sensor is a silicon photovoltaic cell which has withstood repeated high temperature bake-out cycles at 375°C. The sensor can be used inside vacuum systems on earth or in extremely low pressure environments in space and thus eliminates the need to measure through sight glasses.

PRECISION SAMPLE-AND-HOLD STORES VOLTAGE FOR A WEEK

B. K. LUNDE and F. A. SCHMIDT

Electronics 49: 120 (1976)

Abstract--A voltage can be sampled and held for a week or more with at least 99.9% precision by an analog-to-digital converter followed by a digital-to-analog converter. This circuit is useful in automating the electrotransport process for purifying metals. The a-d converter is triggered when the voltage is sampled, and its output is used by the d-a converter to set a programmable power supply.

Mechanical Properties

DETERMINING FULL-FIELD STRAIN DISTRIBUTIONS IN HOT ROLLED BILLETS BY SIMULATION

G. P. Burger, A. K. OYINLOLA, and T. E. SCOTT

Met. Engr. Quarterly p. 21, (May 1976)

Abstract--An experimental technique, termed photoplasticity, was employed to examine the three-dimensional strain distribution in rolled billets.

In particular, a 60:40 mixture of flexible and rigid polyester resins, which exhibits visible light birefringence at strains beyond the elastic limit, was used as the photoplastic material. When deformed at 40°C, this material simulates, at least in the first approximation, characteristics of aluminum when it is deformed at about 425°C. Furthermore, distribution of principal shear strains determined from fringe patterns of rolled blocks of the photoplastic material exhibited features which could be related to edge contours known to form during commercial hot rolling of aluminum. This relatively new technique offers exciting investigative possibilities in the field of deformation processing.

STRAIN RATE SENSITIVITY IN NICKEL-COPPER-CARBON ALLOYS FROM 77K TO 523K

R.P. ZERWEKH and T. E. SCOTT

Proceedings Second International Conference on Mechanical Behavior of Materials held August 16-20, 1976. (American Society for Metals: Metals Park, Ohio, 1976) pp. 1816-1820

Abstract--The influence of carbon on the mechanical properties of nickel has been extensively studied. Nakadah and Keh showed that the strain rate sensitivity (SRS) of nickel is significantly influenced by carbon content and that a pronounced SRS maximum develops below room temperature. The amplitude of the maximum in nickel-carbon alloys was strongly dependent on the amount of carbon present.

Blakemore did a detailed study of the Portevin-Le Chatelier (P-L) effect in nickel-copper-carbon alloys. He found the effect to be caused by carbon in the system, and that its nature varied with copper level. Blakemore's investigation, however, did not include consideration of SRS parameter. Therefore, the purpose of the present work was to systematically study the

composition dependence of SRS behavior in the nickel-copper-carbon system, with particular emphasis on the influence of copper.

A NOVEL MODELLING TECHNIQUE FOR HOT FORMING OF METALS

A. K. OYINLOLA, C. P. Burger and T. E. SCOTT

Proceedings Second International Conference on Mechanical Behavior of Materials held August 16-20, 1976. (American Society for Metals: Metals Park, Ohio, 1976) pp. 1999-2003

Abstract--Improvements in the design of primary hot-working processes such as upset forging, billet rolling and others have been deterred by a lack of knowledge of the internal strain distributions and a need for reliable tool-workpiece interface friction data relevant to commercial practice. For example, Orowan's theory of rolling apparently is the best available but it does not permit the calculation or prediction of internal strain distributions. The latter are important from the point of view that most rolling defects such as edge cracks, undesirable edge contours, alligatoring etc. are caused by secondary stresses resulting from non-uniform three dimensional internal strains. Experimental and analytical methods for obtaining the internal strain distributions incurred during rolling all have important shortcomings.

In regard to tool-workpiece interface friction, it is worth noting that an experimental technique which provides friction data under conditions closely approximating commercial practice has been developed recently. The technique involves the measurement of the change of internal diameter of compressed or upset forged rings. No knowledge of flow stress or compression load is necessary. Several analytical treatments of the deformation involved have been reported. However, certain assumptions required to carry out the analyses have not received experimental evaluation.

The purpose of this present investigation was to attempt an experimental determination of the full-field strain distribution in rolled billets and compressed rings by a simulation method using a photoplastic material.

ELASTIC PROPERTIES OF SOME $Gd_2O_3-HfO_2$ COMPOSITIONS
S. L. DOLE and O. HUNTER, Jr.
J. Nucl. Materials 59: 207 (1976)

Abstract--Gadolinium has the highest neutron capture cross section of all the elements making it a potential material for nuclear reactor control. The elastic moduli and thermal expansion of Gd_2O_3 doped with 0 to 20 mol% HfO_2 were determined. The moduli were determined by the sonic resonance technique over the temperature range from 25 to 1550°C. Additions of HfO_2 had little effect on thermal expansion but significantly increased the elastic moduli. Additions of HfO_2 also increased the sinterability of Gd_2O_3 by inhibiting grain growth. Undoped Gd_2O_3 showed an anomalous elastic behavior that can be attributed to the formation of microcracks while HfO_2 doped Gd_2O_3 did not show this behavior.

PROTON-BOMBARDMENT-INDUCED BLISTERING OF VANADIUM
P. J. HULTGREN and T. E. SCOTT
J. Appl. Phys. 47: 4394 (1976)

Abstract--Samples of annealed and severely cold-rolled vanadium were bombarded at room temperature with 150-keV H^+ ions at fluxes from 1.2×10^{15} to $1.2 \times 10^{16} H^+/cm^2 sec$ to doses of from 3.6×10^{17} to $3.2 \times 10^{19} H^+/cm^2$. All samples irradiated to doses greater than $1.1 \times 10^{19} H^+/cm^2$ exhibited blistering in spite of the fact that temperatures never exceeded the peak miscibility gap temperatures below which vanadium hydride is stable with respect to gaseous hydrogen even at low hydrogen partial pressures.

Niobium also blistered under similar conditions. This unexpected observation must be reconciled by any acceptable theory of radiation blistering.

POROSITY DEPENDENCE OF ELASTIC PROPERTIES OF POLYCRYSTALLINE CUBIC Lu_2O_3

O. HUNTER, Jr., and GEORGE E. GRADDY, Jr.
J. Am. Ceram. Soc. 59: 82 (1976)

Abstract--This work is part of a continuing investigation of the elastic properties of the rare-earth oxides. No data have been published on the porosity dependence of the elastic properties of Lu_2O_3 although the temperature dependence has been studied.

MECHANICAL PROPERTIES OF POLYCRYSTALLINE CERIUM FROM 78 TO 525 K

C. V. OWEN and T. E. SCOTT
J. Less-Common Metals 46: 151 (1976)

Abstract--Flow-stress temperature dependence, strain-rate sensitivity strain-hardening behavior and ductility of cerium were determined from 78 to 525 K at strain rates of 0.005, 0.01, 0.1 and 1.0 min^{-1} . Effects of the transformations between the allotropic forms α , β and γ on the deformation characteristics of cerium were examined. The results are presented and the effects of phase changes are discussed.

EFFECT OF COPPER, TIN, NICKEL, AND CHROMIUM ON MECHANICAL PROPERTIES OF LOW-CARBON STEEL

C. V. OWEN, F. A. SCHMIDT and O. N. CARLSON
Metals Tech. 3: 441 (1976)

Abstract--The effects of those impurities most commonly found in scrap steel on the mechanical properties of low-carbon steel were investigated. The yield and tensile strengths, uniform elongation, strain-hardening exponent, and normal anisotropy ratio were determined as a function of copper, nickel, tin, and chromium content. Attempts to correlate the formability

of steel sheet with changes in these properties are described. Emphasis is placed on the use of the normal anisotropy ratio and the strain-hardening exponent for predicting total formability performance. The results of these tests indicate that tin is most detrimental to the formability of mild steel and that appreciable amounts of copper, nickel, and chromium can be tolerated with relatively few adverse effects.

EFFECTS OF TEMPERATURE AND MICROSTRUCTURE ON THE ELASTIC PROPERTIES OF SELECTED Eu_2O_3 - HfO_2 COMPOSITIONS

R. R. SUCHOMEL and O. HUNTER, Jr.
J. Am. Ceram. Soc. 59:149 (1976)

Abstract--Europium sesquioxide is of interest as a control material for reactors because it has several large-cross-section isotopes which are formed successively on neutron capture. Elastic properties of Eu_2O_3 and selected Eu_2O_3 -rich Eu_2O_3 - HfO_2 compositions were investigated by the sonic technique from room temperature to 1500°C. Sintered monoclinic Eu_2O_3 was found to have anomalously low room temperature moduli and to exhibit hysteresis on thermal cycling. Fine-grained hot-pressed Eu_2O_3 , as well as sintered specimens that contained at least 6 mol% HfO_2 did not exhibit these anomalous characteristics.

HfO_2 AND Ta_2O_5 AS GRAIN GROWTH INHIBITORS IN Eu_2O_3

R. R. SUCHOMEL, R. S. COOK, M. F. BERARD and O. HUNTER, Jr.
J. Nucl. Materials 61: 99 (1976)

Abstract--Because of the high neutron capture cross section for five consecutive europium isotopes, Eu_2O_3 is of interest as a control material for nuclear reactors. A tendency toward excessive grain growth degrades its mechanical properties. Small amounts of HfO_2 and Ta_2O_5 were added

to the Eu_2O_3 in attempts to suppress this grain growth. Three at.% substitution of Hf for Eu suppressed the grain size from approximately 100 μm for pure Eu_2O_3 to 6 μm when the specimens were fired at 1800°C in air for one hour. Three at.% substitution of Ta for Eu suppressed the grain size from 440 μm for pure Eu_2O_3 to 10 μm when the specimens were fired at 1900°C in a vacuum for 1 h.

Physical Properties

SPECIFIC HEAT OF COMPOSITE SUPERCONDUCTORS IN THE PROXIMITY-EFFECT REGIME

A. J. BEVOLO, E. D. GIBSON, J. D. VERHOEVEN, and D. K. FINNEMORE
Phys. Rev. B 14: 114 (1976)

For abstract see Superconductivity, page 51.

ELECTRICAL RESISTIVITY AND MAGNETIC SUSCEPTIBILITY OF β -CERIUM FROM 2 TO 300 K

P. BURGARDT, K. A. GSCHNEIDNER, Jr., D. C. KOSKENMAKI, D. K. FINNEMORE, J. O. MOORMAN, S. LEGVOLD, C. STASSIS, and T. A. VYROSTEK
Phys. Rev. B 14: 2995 (1976)

For abstract see Magnetic Properties of Solids, page 46.

MAGNETO-RESISTIVITY OF BETA-CERIUM

P. BURGARDT, S. LEGVOLD, J. H. QUEEN and K. A. GSCHNEIDNER, Jr.
Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 527-528

For abstract see Magnetic Properties of Solids, page 47.

ELASTIC CONSTANTS OF NEODYMIUM SINGLE CRYSTALS IN THE TEMPERATURE RANGE 4.2-300°K

J. D. GREINER, D. M. SCHLADER, O. D. McMASTERS, K. A. GSCHNEIDNER, Jr., and J. F. SMITH
J. Appl. Phys. 47: 3427 (1976)

Abstract--The elastic constants of a single crystal of the double hcp allotrope of neodymium have been measured over the temperature range

4.2–300 K. The magnetic orderings which occur in neodymium near 7.5 and 19 K are readily evident as cusps in the temperature dependences of some of the directly measured ultrasonic wave velocities as well as in the associated elastic constants, and the character of the magnetic interactions is reflected in the differing effects on the various elastic constants. Comparison of the elastic constants of neodymium with those of seven other rare earths shows a trend with atomic number which is similar to trends which have been observed in other physical properties.

RHOMBOHEDRAL DISTORTION IN HIGHLY MAGNETOSTRICTIVE LAVES PHASE COMPOUNDS

A. E. Clark, J. R. Cullen, O. D. McMASTERS and E. R. Callen
Magnetism and Magnetic Materials -- 1975, eds. J. J. Becker, G. H. Lander and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 192–193

Abstract--A model is presented which produces a magnetostrictively driven rhombohedral distortion (λ_{111}) in cubic diamond-like structures. No tetragonal magnetostrictive distortion (λ_{100}) is allowed, which is consistent with the experimental observation, $\lambda_{111} \gg \lambda_{100}$. From x-ray and single crystal measurements we find $|\lambda_{111}/\lambda_{100}| > 600$ for DyFe_2 . Rhombohedral distortions (λ_{111}) are examined in the ternary $\text{Tb}_{1-x}\text{Gd}_x\text{Fe}_2$, $\text{Tb}_{1-x}\text{Y}_x\text{Fe}_2$ and $\text{Tb}_{1-x}\text{Dy}_x\text{Fe}_2$ systems by x-ray methods. The single-ion nature of the giant Tb magnetostriction in TbFe_2 is verified.

KONDO SCATTERING IN A PURE METAL-- β CERIUM: I. EXPERIMENTAL

K. A. GSCHNEIDNER, Jr., P. BURGARDT, S. LEGVOLD, J. O. MOORMAN, T. A. VYROSTEK and C. STASSIS
 J. Phys. F: Metal Phys. 6: L49 (1976)

Abstract--The electrical resistivity of DHCP β Ce has been found to be anomalously large above 60 K and to exhibit an order of magnitude drop below 20 K. The magnetic susceptibility exhibits a Curie-Weiss behaviour

above 40 K, and magnetic ordering occurs at ~ 13 K. The large resistivity is thought to be due to Kondo-like spin flip scattering which, at low temperatures, is quenched by the internal field associated with magnetic ordering.

KONDO SCATTERING IN A PURE METAL-- β CERIUM: II. THEORETICAL
S. H. LIU, P. BURGARDT, K. A. GSCHNEIDNER, Jr., and S. LEGVOLD
J. Phys. F: Metal Phys. 6: L55 (1976)

See abstract under Theoretical Research III, page 68.

GEOMETRIC SURFACE RELIEF AND THE ALLOTROPIC TRANSFORMATION IN IRON
K. R. Kinsman, R. H. Richman and J. D. VERHOEVEN
J. Mat. Sci. 11: 1487 (1976)

Abstract--Geometric surface relief effects have been observed in association with the $\gamma \rightarrow \alpha$ allotropic transformation in iron. The selected area electron channelling pattern technique has been used to establish that tent-shaped geometric relief effects, common to single α precipitate plates in Fe-C and Fe-C-X alloys, are also associated with similar single crystal morphologies in pure iron. These experimental observations extend to the allotropic transformation in iron the same rationale for the relationship of interfacial structure to surface relief effects that is known to apply in the instance of precipitation reactions. In addition it provides support for an earlier proposal that "massive" transformations can be subject to the same crystallographic constraints as precipitation processes.

THE ROCKWELL C HARDNESS OF QUENCHED HIGH-PURITY IRON-CARBON ALLOYS CONTAINING 0.09 TO 1.91% CARBON
A. LITWINCHUK, F. X. KAYSER, H. H. BAKER and A. Henkin
J. Mat. Sci. 11: 1200 (1976)

Abstract--The Rockwell C hardnesses of thirteen high-purity iron-carbon alloy specimens that had been brine-quenched from temperatures in

the austenite region to room temperature were measured. The hardness versus wt % C curve exhibits a maximum value of $\sim 65.5 R_c$ near 0.9% C. The decrease in hardness at carbon concentrations $> 0.9\%$ is the result of a rapid increase in the volume fraction of retained austenite. Attention is called to the desirability of using these or similar data in materials texts to illustrate this structure-property relationship.

PHASE DIAGRAM AND THERMODYNAMIC PROPERTIES OF THE YTTRIUM-ZINC SYSTEM

J. T. MASON and P. CHIOTTI
Met. Trans. A 7A: 287 (1976)

Abstract--The phase relations of the yttrium zinc system have been reexamined. A total of eight compounds have been identified by differential thermal analysis, metallographic and x-ray diffraction techniques. The three compounds YZn , YZn_2 and $YZn_{8.5}$ melt congruently at 1105, 1080 and 890°C, respectively. The compounds YZn_3 , $YZn_{3.67}$, $YZn_{4.46}$, YZn_6 and YZn_{12} all decompose peritectically at 905, 896, 882, 872 and 685°C, respectively. Three eutectics were found at 875°C and 23.2 wt pct Zn (29.12 at. pct), 1015°C and 51 wt pct Zn (59 at. pct) and at 863°C and 82 wt pct Zn (86 at. pct). A polymorphic transformation was observed in the YZn_2 compound that proceeds at 750°C in the yttrium rich region but drops to approximately 630°C in the zinc rich region. The thermodynamic properties of the intermetallic compounds have been determined using the dewpoint method to measure the vapor pressure of zinc. The standard free energy relations vary from $\Delta G^\circ (YZn) = 24,020 + 8.76T$ to $\Delta G^\circ (YZn_{12}) = -85,940 + 48.61T$ cal/mole.

PHASE BOUNDARIES AND THERMODYNAMIC ANALYSIS OF THE RARE-EARTH-RICH ALLOYS IN THE La-Tl AND Pr-In SYSTEMS

O. D. McMASTERS and K. A. GSCHNEIDNER, Jr.

J. Less-Common Metals 44: 281 (1976)

Abstract--The phase boundaries in the rare-earth-rich portions of the lanthanum-thallium and praseodymium-indium systems were determined using differential thermal methods. The solid solubility of Tl in b.c.c. γ -La is 11.0 at.% at the 655°C eutectic temperature and that in f.c.c. β -La is 1.9 at.% at the 640°C eutectoid temperature. The solid solubility of In in b.c.c. β -Pr is 9.8 at.% at the 825°C eutectic temperature while that in d.h.c.p. α -Pr is 5.6 at.% at the 725°C eutectoid temperature. The first La-rich compound, La_3Tl , decomposes peritectoidally at 645°C and La_2Tl melts peritectically at 900°C. The compound Pr_3In decomposes peritectically at 930°C.

The thermodynamic analyses data for these alloys were compared with those reported for the La-In and Pr-Tl systems.

THE PRASEODYMIUM-LEAD SYSTEM

O. D. McMASTERS and K. A. GSCHNEIDNER, Jr.

J. Less-Common Metals 45: 275 (1976)

Abstract--X-ray diffraction, differential thermal, and metallographic methods, were used to establish the praseodymium-lead phase diagram. Eutectic reactions occur at 9.3 at.% Pb and 824°C, at 55.5 at.% Pb and 1145°C, at 62.5 at.% Pb and 1085°C and at greater than 99.5 at.% Pb and 325°C. The intermetallic compounds Pr_3Pb , Pr_5Pb_4 , $\text{Pr}_{11}\text{Pb}_{10}$ and PrPb_2 decompose peritectically at 860, 1455, 1365 and 1090°C, respectively. Pr_5Pb_3 , Pr_3Pb_4 and PrPb_3 melt congruently at 1495, 1180 and 1120°C, respectively. The crystal structure data are given for these compounds. The solid solubility of

lead in praseodymium is 3.5 at.% Pb at the 824°C eutectic temperature. The alloying characteristics of some of the Pr-Pb alloys are compared with those in the La-Pb and Pu-Pb systems.

INTERDIFFUSION IN THE SYSTEM SrF_2 - BaF_2

R. W. SCHEIDECKER and M. F. BERARD

J. Am. Ceram. Soc. 59: 431 (1976)

Abstract--A microprobe study of interdiffusion between 1033° and 1238°C in the system SrF_2 - BaF_2 was conducted using single crystals. The interdiffusion coefficient, $\bar{D}$, generally decreased with increasing SrF_2 concentration, but the composition dependence of $\bar{D}$ decreased with decreasing temperature. Extrapolation of $\bar{D}$ values to infinite dilution allowed the impurity cation self-diffusion coefficients:

$$\begin{aligned} \bar{D}_{\text{Sr in BaF}_2} &= \left(4.61^{+1.18}_{-0.94} \right) \times 10^3 \exp \\ &\left(- \frac{86.4 \pm 4.4 \text{ kcal/mol}}{RT} \right) \text{ cm}^2/\text{s} \\ \bar{D}_{\text{Ba in SrF}_2} &= \left(3.01^{+1.23}_{-0.88} \right) \times 10^3 \exp \\ &\left(- \frac{92.0 \pm 6.8 \text{ kcal/mol}}{RT} \right) \text{ cm}^2/\text{s} \end{aligned}$$

The values for $\bar{D}_{\text{Sr}}$ in BaF_2 are in excellent agreement with tracer results. An analysis of the activation energies for cations diffusing in alkaline-earth fluorides shows a direct correlation between constriction ratio and migration energy for a single ion diffusing in different fluorides. An apparent anomaly arises when attempting to correlate migration energy with structural information for different cations diffusing in the same fluoride.

THERMODYNAMIC PROPERTIES OF BINARY LITHIUM SYSTEMS -- A REVIEW

J. F. SMITH and Z. MOSER

J. Nucl. Mater. 59: 158 (1976)

Abstract--The available thermodynamic data for binary systems of lithium have been critically reviewed and summarized. Some data are included for forty-three solid intermediate phases and for sixteen liquid solutions distributed among twenty-nine systems. Information was evaluated primarily on the basis of consistency, but in cases of conflicting data the relative capabilities of the experimental techniques were weighed.

LOW TEMPERATURE HEAT CAPACITY OF ELECTROTRANSPORTED SCANDIUM

T. -W. E. TSANG, K. A. GSCHNEIDNER, Jr., and F. A. SCHMIDT
Solid State Comm. 20: 737 (1976)

Abstract--The heat capacity of two scandium samples containing 1.6 and <5 ppm atomic Fe was measured from 1 to 20 K. The weighted values for γ and θ_D are: 10.340 ± 0.018 mJ/g-at. K² and 346.1 ± 0.9 K, respectively. This is the first time anyone has obtained the same heat capacity results on two different scandium samples. The iron impurity concentration appears to be critical.

LOW TEMPERATURE HEAT CAPACITY OF SCANDIUM AND SCANDIUM ALLOYS

T. -W. E. TSANG, K. A. GSCHNEIDNER, Jr., and F. A. SCHMIDT
Proceedings of the 12th Rare Earth Research Conference, ed. C. E. Lundin
(Denver, Colorado: University of Denver and Denver Research Institute, 1976)
Vol. II pp. 847-854

Abstract--The heat capacity of several scandium samples containing between 1.6 and 10,000 ppm atomic Fe was measured from 1 to 20 K. Samples containing more than 30 ppm Fe exhibit an anomaly between 1 and 1.5 K, but two scandium samples containing less than 5 ppm Fe did not show

any anomalies. For these two samples the weighted values for γ and θ_D are:
 $10.340 \pm 0.018 \text{ mJ/g-at. K}^2$ and $346.1 \pm 0.9 \text{ K}$, respectively.

REDETERMINATION OF THE HEAT CAPACITY OF SINGLE PHASE β -CERIUM

T.-W. E. TSANG, K. A. GSCHNEIDNER, Jr., D. C. KOSKENMAKI and J. O. MOORMAN
 Phys. Rev. B 14: 4447 (1976)

Abstract--The heat capacity of a carefully characterized β -Ce sample was measured from 1 to 20 K. The present results are in excellent agreement with the earlier data from 1.5 to 12.8 and 15.8 to 20 K. Between 12.8 and 15.8 the present results are ~4% higher than the earlier values and this is thought to be due to less lattice strains in the present sample. The magnetic heat capacity below 1.33 K exhibits an exponential behavior, yielding an energy gap of $1.41 \pm 0.02 \text{ K}$.

HfO₂ AND Ta₂O₅ AS GRAIN GROWTH INHIBITORS IN Eu₂O₃

R. R. SUCHOMEL, R. S. COOK, M. F. BERARD and O. HUNTER, Jr.
 J. Nucl. Materials 61: 99 (1976)

See abstract under Mechanical Properties, page 26.

A SPECIMEN FOR EVALUATING THE AREA OF SACPs

J. D. VERHOEVEN and H. H. BAKER
 J. Mat. Sci. 11: 388 (1976)

Abstract--The preparation of a specimen which is well suited for the evaluation of the area from which electron channelling patterns originate is described. The specimen is a cast Al-Ge alloy which contains many small Ge particles in the size range of 3 to 15 μm . These particles are present in a matrix of a fine eutectic microstructure and hence patterns are obtained from the particles and not the matrix. Casting and polishing procedures are described.

EVALUATION OF A LaB_6 CATHODE ELECTRON GUN

J. D. VERHOEVEN and E. D. GIBSON

J. Phys. E 9: 65 (1976)

Abstract--The brightness of the lanthanum hexaboride, LaB_6 , cathode electron gun of the Stereoscan S-4 scanning electron microscope has been evaluated. This gun is an indirectly heated Broers type of LaB_6 gun design, and the several variables which affect its brightness have been evaluated using a cage device for the brightness measurements. The results indicate that when proper operating conditions are employed the LaB_6 brightnesses are of the order of 15 to 20 times that of tungsten operated at 40 h life conditions, and that single crystal cathodes are more reliable for producing high brightnesses.

INFLUENCE OF CRYSTALLOGRAPHY AND PURITY ON BRIGHTNESS OF LaB_6 CATHODES

J. D. VERHOEVEN, E. D. GIBSON and M. A. NOACK

J. Appl. Phys. 47: 5105 (1976)

Abstract--The brightness of single-crystal cathodes of LaB_6 oriented in the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions and six other random directions has been measured. The $\langle 111 \rangle$ cathodes produced currents and brightnesses significantly lower than all other orientations. The other orientations studied produced maximum brightnesses in the range $0.7\text{--}1.0 \text{ MA/cm}^2\text{sr}$, although the $\langle 100 \rangle$ orientation consistently produced currents higher than other orientations and brightnesses as high or higher than most orientations. A change in impurity level from 1540 ppm to less than 1 ppm had no statistical effect on brightness for crystals of the same orientation.

AN ARC FLOATING ZONE TECHNIQUE FOR PREPARING SINGLE CRYSTAL LANTHANUM HEXABORIDE

J. D. VERHOEVEN, E. D. GIBSON, M. A. NOACK and R. J. CONZEMIUS
J. Crystal Growth 36: 115 (1976)

Abstract--An arc floating zone technique has been developed for producing LaB_6 . The technique consistently produces single crystals which nucleate and grow with essentially random crystallographic orientations. Chemical analyses show that very effective purification is obtained, contamination from the tantalum electrode material does not occur, and stoichiometry of the LaB_6 is maintained.

THE METALLURGY OF RETICULATED SILVER SHEET

JOHN D. VERHOEVEN and ROHIT K. TRIVEDI
Metallography 9: 367 (1976)

Abstract--Reticulation is a process used by artists in producing attractive rippled surfaces on rolled sheet of Ag-Cu alloys. A metallographic study of the process is presented which shows that a subsurface layer of CuO formed by internal oxidation plays a key role in the process. Based on this study, two processes more simple than the conventional process are presented for preparing reticulation sheet.

Radiation Effects

DEFECT CLUSTERS IN NEUTRON-IRRADIATED VANADIUM CONTAINING OXYGEN

R. BAJAJ and M. S. WECHSLER
Met. Trans. A 7A: 351 (1976)

Abstract--Single crystal samples of high-purity vanadium containing 95, 300, and 500 wt ppm oxygen were irradiated at 95°C in the Ames Laboratory Research Reactor to a dose of 1.4×10^{19} neutrons/cm² ($E > 1$ MeV). The

density and size distribution of radiation-produced defect clusters were analyzed by transmission electron microscopy in as-irradiated and post-irradiation-annealed material. The defect cluster density was observed to increase with increasing oxygen concentration while the average defect cluster size decreased. Upon post-irradiation annealing the density decreased and the average size increased, but higher annealing temperatures were required for higher oxygen material. The results are discussed in terms of the nucleation of defect clusters at oxygen atoms and small oxygen-atom aggregates. The increased stability against annealing of higher oxygen vanadium is believed to be due to the greater segregation of oxygen at the defect clusters.

THE INFLUENCE OF OXYGEN IMPURITY ATOMS ON DEFECT CLUSTERS AND RADIATION HARDENING IN NEUTRON-IRRADIATED VANADIUM

R. BAJAJ and M. S. WECHSLER
Fundamental Aspects of Radiation Damage in Metals Proc. International Conference held Gatlinburg, TN, October 6-10, 1975. eds. M. T. Robinson and F. W. Young, Jr., (Oak Ridge, Tennessee: Energy Research and Development Administration, 1976) pp. 1010-1017 (CONF-751006)

Abstract--Single crystal TEM samples and polycrystalline tensile samples of vanadium containing 60-640 wt ppm oxygen were irradiated at about 100°C to about 1.3×10^{19} neutrons/cm² ($E > 1$ MeV) and post-irradiation annealed up to 800°C. The defect cluster density increased and the average size decreased with increasing oxygen concentration. Higher oxygen concentrations caused the radiation hardening and radiation-anneal hardening to increase. The observations are consistent with the nucleation of defect clusters by small oxygen or oxygen-point defect complexes and the trapping of oxygen at defect clusters upon post-irradiation annealing.

RADIATION EMBRITTLEMENT OF METALS AND ALLOYS

M. S. WECHSLER

Fundamental Aspects of Radiation Damage in Metals Proc. International Conference held Gatlinburg, TN, October 6-10, 1975, eds. M. T. Robinson and F. W. Young, Jr. (Oak Ridge, Tennessee: Energy Research and Development Administration, 1976) pp. 991-1009. (CONF-751006)

Abstract--Radiation embrittlement refers to enhanced fracture susceptibility and reduction in load-carrying capacity exhibited by irradiated metals. Three types of radiation embrittlement are identified: (1) radiation embrittlement in nominally ductile metals, (2) radiation embrittlement in metals that undergo a ductile-brittle transition, and (3) high-temperature grain boundary embrittlement. This paper deals with type (1) and, more briefly, type (2) radiation embrittlement.

Radiation embrittlement in nominally ductile metals is characterized by the premature onset of plastic instability, which causes a sharp decrease in the macroscopic plastic strain that the material can sustain before necking (uniform strain) and breaking (fracture strain). Dislocation channeling seems to be largely responsible and experimental results are reviewed. The origin of dislocation channeling is discussed.

Irradiated metals that exhibit a ductile-brittle transition show an increase in the transition temperature but the nature of the transition (shear to cleavage fracture) does not appear to be greatly altered. A key factor is the temperature dependence of yielding and how it is affected upon irradiation. Impurities exert an influence on the stability of radiation-produced defect clusters and thus can alter the amount of radiation embrittlement experienced upon irradiation at somewhat elevated temperatures.

In general, radiation embrittlement appears to stem mostly from changes in plastic properties (particularly in the trend toward more dynamic and inhomogeneous plastic deformation) rather than from changes in the inherent fracture process.

SUPPRESSION OF VOID FORMATION IN NICKEL BY A DYNAMIC TRAPPING MECHANISM

S. M. SORENSON and C. W. CHEN

Fundamental Aspects of Radiation Damage in Metals Proc. International Conference held Gatlinburg, TN, October 6-10, 1975, eds. M. T. Robinson and F. W. Young, Jr. (Oak Ridge, Tennessee: Energy Research and Development Administration, 1976) pp. 1213-1220. (CONF-751006)

Abstract--The effect of carbon on void formation in high purity nickel under neutron irradiation to four fluences ranging from 4×10^{18} to 2×10^{20} n/cm² ($E > 0.1$ MeV) at 500°C was investigated using transmission electron microscopy. In samples containing up to 84 wt ppm C, cubic voids were observed, and the void size tended to increase with increasing C content, while the void density decreased at much greater rates. Consequently, the associated swelling was seen to be steadily reduced. In samples containing 600 ppm C, void formation was completely suppressed, and an irradiation-induced dissolution of graphite precipitates occurred. The suppression of void formation in the irradiated Ni is attributed to an effective trapping mechanism associated with the interstitial C atoms in solution. Quantitative analyses on the size and density of voids reveal that the suppressing effect of C is mainly on void nucleation, not on growth. This trapping mechanism is considered to be dynamic in nature because the traps served by the C atoms can move through the lattice rapidly during irradiation until they are anchored in defect complexes.

Solid State Physics

NEUTRON SCATTERING

POLARIZED-NEUTRON STUDY OF THE COHERENT PARAMAGNETIC SCATTERING AMPLITUDE OF METALLIC ERBIUM

C. STASSIS, G. R. KLINE, A. J. Freeman and J. P. Desclaux
Phys. Rev. B 13: 3916 (1976)

Abstract--Polarized-neutron techniques have been used to measure the coherent paramagnetic scattering amplitude of high-purity single crystals of metallic erbium at 300 K. The angular dependence of the coherent-scattering amplitude has been determined with the external magnetic field ($H = 22$ kOe) applied parallel as well as perpendicular to the $\underline{c}$ axis of the crystal. It has been found that the angular dependence of the scattering amplitude for $\vec{H} \parallel \vec{c}$ as well as $\vec{H} \perp \vec{c}$ is in good agreement, except at small scattering angles, with the $4f$ -electron magnetic form factor calculated using relativistic Dirac-Fock wave functions. At small scattering angles the experimental points were found to be systematically higher than the theoretical curves obtained by least-square fitting of the calculated $4f$ -electron form factor to the large-angle experimental points. This small-angle contribution, attributed to the polarization of the conduction bands of erbium, has an unusual angular dependence; it is different from either a $5d$ or $6s$ atomic form factor and exhibits a non-negative oscillatory character.

MAGNETIC SCATTERING OF NEUTRONS BY A RELATIVISTIC ATOM IN
THE ℓ^N CONFIGURATION

C. STASSIS and H. W. DECKMAN

Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander
and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 274-275

Abstract--We examined the magnetic scattering of neutrons by an atom described by a relativistic Hamiltonian. It is shown that the magnetic scattering amplitude can be expressed in terms of (relativistic) matrix elements of relativistic magnetic and electric multipole operators. An effective magnetic scattering amplitude is then defined so that a relativistic result is obtained by taking matrix elements of this operator between non-relativistic states of the atom. Quite generally the effective magnetic scattering amplitude can be expressed in terms of relativistic radial integrals and the Racah tensors $W^{(0,k)k}$ and $W^{(1,k')k}$ ($k' = k, k \pm 1$). For simplicity, explicit expressions for the relativistic radial integrals are given for the experimentally important case of neutron scattering by an atom in the ℓ^N configuration.

COMMENT ON THE REDUCTION OF AN IMPORTANT 9-j SYMBOL

C. STASSIS and S. A. WILLIAMS

J. Math. Phys. 17: 480 (1976)

See abstract under Nuclear Physics, page 11.

MAGNETIC SCATTERING OF NEUTRONS BY ATOMS

C. STASSIS and H. W. DECKMAN

J. Phys. C: Solid State Phys. 9: 2241 (1976)

Abstract--We examine the magnetic scattering of neutrons by an atom or ion possessing both a spin and orbital magnetic moment. For an atom in the 1^n electronic configuration the magnetic scattering amplitude is determined by matrix elements of even-order electric and odd-order magnetic multipoles, whose order of multipolarity k is less than or equal to $2l + 1$. The calculation

of the matrix elements of these multipoles is separated into evaluating radial matrix elements and matrix elements of the Racah tensors $\underline{W}^{(0,\underline{k})}$ and $\underline{W}^{(1,\underline{k}')}$ where $\underline{k}'$ is an even integer less than or equal to $2\underline{1}$. The calculation of the matrix elements of these tensors is considerably simplified by selection rules based on the groups $\underline{Sp}(4\underline{1} + 2)$, $\underline{R}(2\underline{1} + 1)$, $\underline{R}(3)$ and in the case of f-electrons, the special group $\underline{G}_2$. It is shown that, in the case of elastic scattering by an atom or ion whose state is a single Russell-Saunders state, the magnetic scattering amplitude can be written in the conventional form $\underline{p}(\underline{q})\underline{p}_m \cdot \sigma$. General expressions for the amplitude $\underline{p}(\underline{q})$ as well as the elastic magnetic form factor are obtained. The evaluation of the coherent magnetic scattering amplitude by an atom in a magnetic field is discussed, and the small- $\underline{q}$ approximation to the elastic magnetic scattering is considered. The formalism is illustrated for the important case of d- and f-electrons. The generalization of the formalism to the case of mixed atomic configurations is examined in some detail.

MAGNETIC SCATTERING OF NEUTRONS BY A RELATIVISTIC ATOM
 C. STASSIS and H. W. DECKMAN
 Phys. Rev. B 13: 4934 (1976)

Abstract--We examined the magnetic scattering of neutrons by an atom described by a relativistic Hamiltonian. It is shown that the magnetic-scattering amplitude can be expressed in terms of relativistic magnetic and electric multipole operators. An effective magnetic-scattering amplitude is then defined so that a relativistic result is obtained by taking matrix elements of this effective operator between nonrelativistic states of the atom. It is shown that the effective magnetic-scattering amplitude can be expressed in terms of relativistic radial integrals and the generalized Racah tensors

$\underline{W}^{(0,\underline{k})\underline{k}}(\underline{n}\underline{l}, \underline{n}'\underline{l}') \text{ and } \underline{W}^{(1,\underline{k}')\underline{k}}(\underline{n}\underline{l}, \underline{n}'\underline{l}') \text{ } (\underline{k}' = \underline{k}, \underline{k} \pm 1)$. The relativistic radial integrals can be evaluated using one-electron radial wave functions, obtained by Hartree-Fock-Dirac calculations. The matrix elements of the Racah tensors can be obtained by standard techniques and their evaluation is considerably simplified by selection rules based on the symmetry properties of the atomic states. The formalism has been applied to the magnetic scattering of neutrons by an atom in the $\underline{l}^N$ electronic configuration. In this case, explicit expressions for the relativistic radial integrals have been derived, and the nonrelativistic limit of the effective magnetic-scattering amplitude has been examined.

ASPHERICITY IN THE MAGNETIZATION DISTRIBUTION OF HOLMIUM

G. P. Felcher, G. H. Lander, T. Arai, S. K. SINHA and F. H. SPEDDING
Phys. Rev. B 13: 3034 (1976)

Abstract--In a spiral magnetic structure, an aspherical magnetic moment distribution around the ions gives rise to a new set of diffraction lines indexed as third-order satellites. Neutron-diffraction measurements have been made on single crystals of holmium and a $\text{Ho}_{0.9}\text{Sc}_{0.1}$ alloy to determine the magnetic structures as a function of temperature, and measure the intensities of the third-order satellites. From these intensities the experimental asphericity of the magnetization density is compared to that calculated with a single-ion model. The agreement between theory and experiment is qualitative; the experimental intensities being larger by a factor of ~ 1.5 . The temperature dependence of the third-order satellite is in good agreement with a simple model proposing exchange splitting of the free-ion multiplet, with a negligible crystal-field interaction.

CONCENTRATION-DEPENDENT KOHN EFFECT IN CUBIC TUNGSTEN BRONZES

W. A. KAMITAKAHARA, B. N. HARMON, J. G. TAYLOR, L. KOPP,
H. R. SHANKS and J. Rath
Phys. Rev. Lett. 36: 1393 (1976)

Abstract--Inelastic neutron scattering measurements on single crystals of cubic Na_xWO_3 reveal a large concentration-dependent Kohn anomaly in the [100] longitudinal acoustic-phonon dispersion curve. The results demonstrate the two-dimensional character of the Fermi surface, support the rigid-band model for $0.56 < x < 0.83$, and conflict with the percolation model which has just recently been proposed to explain the transport properties of the tungsten bronzes.

EXPERIMENTAL RESEARCH

I. MAGNETIC PROPERTIES OF SOLIDS

KONDO SCATTERING IN A PURE METAL -- β CERIUM: I. EXPERIMENTAL

K. A. GSCHNEIDNER, Jr., P. BURGARDT, S. LEGVOLD, J. O. MOORMAN,
T. A. VYROSTEK and C. STASSIS
J. Phys. F: Metal Phys. 6: L49 (1976)

See abstract under Physical Properties page 28.

KONDO SCATTERING IN A PURE METAL -- β CERIUM: II. THEORETICAL

S. H. LIU, P. BURGARDT, K. A. GSCHNEIDNER, Jr., and S. LEGVOLD
J. Phys. F: Metal Phys. 6: L55 (1976)

See abstract under Theoretical Research III, page 68.

SUPERCONDUCTIVITY IN SINGLET La-Pr AND IN NONMAGNETIC La-RARE EARTH ALLOYS

S. LEGVOLD, R. W. GREEN, B. J. BEAUDRY and J. E. OSTENSON
Solid State Comm. 18: 725 (1976)

See abstract under Structure of Materials, page 17.

KONDO EFFECT IN Y-RICH ALLOYS CONTAINING A Ce IMPURITY

T. S. PETERSEN, S. LEGVOLD and P. BURGARDT

Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 366-367

Abstract--Sugawara et al. have found that Ce impurities in some non-magnetic rare earth hosts exhibit the Kondo effect. Maple and Wittig have shown that when pressure is applied to Y-Ce, the Kondo effect disappears, assumedly because the $4f$ level is driven from below to above the Fermi level. In the work reported here, alloy hosts of $Y_x La_{1-x}$ are used to get the slope of the Kondo resistivity as a function of atomic volume for samples containing 2 atomic percent Ce impurity. The slope of the ρ vs. $\ln T$, $(d\rho/d \ln T)$ varies markedly with atomic volume and shows a sharp peak near $x = 0.95$. Furthermore, by using Y-Lu host alloys the Kondo effect will disappear at the atomic volume calculated for the Maple and Wittig result.

MAGNETIC MOMENTS OF FERROMAGNETIC GADOLINIUM ALLOYS

H. W. White, B. J. BEAUDRY, P. BURGARDT, S. LEGVOLD and B. N. HARMON

Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 329-330

Abstract--Saturation magnetization and lattice parameter measurements have been made on samples of polycrystalline and single crystal c-axis gadolinium and on samples of polycrystalline gadolinium alloyed with scandium, yttrium, lutetium, lanthanum, magnesium, ytterbium and thorium. The magnetic measurements were made near 4.2 K in fields up to 30 kOe. Alloy concentrations ranged up to 30 atomic percent. For pure single crystal gadolinium the saturation moment was measured to be $7.63 \pm 0.01 \mu_B$ per gadolinium atom. This result indicates the conduction electron contribution is about 13% higher than the value obtained from earlier measurements. For

polycrystalline gadolinium the saturation moment per atom was found to be $7.555 \pm 0.015 \mu_B$. The excess moment per Gd atom for the polycrystalline alloys fell near a straight line when plotted as a function of the unit cell axes ratio c/a . The c/a ratios ranged from 1.583 to 1.595 and the excess moments were between 0.78 and $0.44 \mu_B$. Surprisingly, there was no correlation of excess moment with atomic volume or with the valence of the solute atoms.

ELECTRICAL RESISTIVITY AND MAGNETIC SUSCEPTIBILITY OF β -CERIUM FROM 2 TO 300 K

P. BURGARDT, K. A. GSCHNEIDNER, Jr., D. C. KOSKENMAKI, D. K. FINNEMORE, J. O. MOORMAN, S. LEGVOLD, C. STASSIS and T. A. VYROSTEK

Phys. Rev. B 14: 2995 (1976)

Abstract--The electrical resistivity and magnetic susceptibility of allotropically pure β -Ce and some two-phase ($\alpha + \beta$ or $\beta + \gamma$) samples, which were predominantly β -Ce, were measured from 2 to 300 K. Because β -Ce transforms to α -Ce between 15 and 50 K, several unusual experimental techniques were used to obtain reliable data. Our results show that the electrical resistivity of β -Ce remains unusually large, $> 50 \mu\Omega\text{cm}$ down to 40 K and below this temperature it drops an order of magnitude. The magnetic susceptibility data show that β -Ce obeys the Curie-Weiss law down to near its Néel temperature, ~ 12.5 K. Low-field susceptibility data, < 800 Oe, show a Néel temperature at 12.5 K and that the magnetic susceptibility near the ordering temperature decreases with increasing field. X-ray metallographic data indicate that when β -Ce transforms to α -Ce the initial growth occurs at the surface and grows inward. The unusual temperature dependence of the electrical resistivity of β -Ce could not be explained by several existing models (band-spin fluctuation or crystalline field) which have been used to

explain large increases in the resistivity for other materials. However, a recently developed model based on Kondo scattering which is quenched by magnetic ordering appears to account for the observed results.

MAGNETO-RESISTIVITY OF BETA-CERIUM

P. BURGARDT, S. LEGVOLD, J. H. QUEEN and K. A. GSCHNEIDNER, Jr.
Magnetism and Magnetic Materials--1975, eds. J. J. Becker, G. H. Lander
 and J. J. Rhyne (New York: American Institute of Physics, 1976) pp. 527-528

Abstract--Longitudinal magneto-resistivity measurements of alloyed pure samples of dhcp cerium were made at temperatures from 4.2 to 90 K in fields up to 80 kOe. The results show negative magneto-resistivity which is typical of field suppression of spin flip scattering. In the vicinity of the Néel temperature complex results were obtained which are interpreted as the interaction of internal fields with the applied field.

ANTIFERROMAGNETISM OF THE α -Mn SYSTEM

W. WILLIAMS, Jr. and J. L. STANFORD
J. Magnetism & Magnetic Materials 1: 271 (1976)

Abstract--The variation of the Néel temperature (T_N) of antiferromagnetic alloys of Mn with 3-d elements has been studied by electrical resistivity measurements. Binary Mn-rich alloys containing Fe, Co, Ni, Ti, Rh, Os, Ir, and Ru were investigated. The results show a strong and systematic dependence on the number of d-electrons of the impurity element. Elements with more d electrons than Mn raise T_N , while those with fewer d electrons depress T_N . The change of T_N per atomic percent impurity also exhibits a striking, non-monotonic dependence on the impurity used. The dependence shows inversion symmetry with impurities around Mn.

To further elucidate the properties of the Mn-rich antiferromagnetic system, a study was made of ternary Mn-rich alloys in the Mn-Fe-Cr,

Mn-Co-Ni, and Mn-V-Ti systems. The results from the Mn-Fe-Cr system are consistent with the rigid-band model, the average number of d-electrons per atom being of primary importance in determining the antiferromagnetism in this system.

Our goal in these studies has been to provide a firm experimental data base upon which future theoretical work can be built. A more detailed understanding of the very intriguing α -Mn magnetic system now awaits further theoretical investigation.

II. NUCLEAR RESONANCE IN SOLIDS

A USEFUL NUCLEAR MAGNETIC RESONANCE LINESHAPE FUNCTION FOR METALLIC SOLIDS

W. C. HARPER and R. G. BARNES
J. Magnetic Resonance 21: 507 (1976)

Abstract--A novel analytic representation for nuclear magnetic resonance (NMR) lineshapes is presented, covering continuously the range from Gaussian to rectangular shape and readily adaptable to computer calculation and data fitting. This function has been found to be very useful in proton NMR studies of hydrogen-storing intermetallic compounds.

A DEUTERON MAGNETIC RESONANCE STUDY OF TANTALUM DEUTERIDES

K. P. ROENKER, R. G. BARNES and H. R. Brooker
Sondordruck Zeit.: Berichte der Deutschen Gesellschaft für physikalische Chemie (früher Zeitschrift für Elektrochemie) 80: 470 (1976)

Abstract--Tantalum deuterides in the composition range $TaD_{0.43}$ – $TaD_{0.76}$ were investigated by means of deuteron nuclear magnetic resonance over the temperature range from 4.2 to 400 K. The β - α phase transition, in the temperature range 320–370 K for these compounds, is sharply defined by

the extinction of the deuteron quadrupole interaction when the cubic α phase is reached. These results are discussed in relation to other determinations of the β - α transition temperature. No other significant changes in the NMR spectrum are observed, down to 4.2 K, at which temperature the quadrupole coupling constants are equal, within the experimental uncertainty, having the value, $e^2 qQ/h = 33.9 \pm 0.7$ kHz, independent of composition. The asymmetry parameter values, however, tend toward zero with increasing deuterium content. It is noted that the thermal width of the β - α transition is increased by high oxygen content of the tantalum metal.

DEUTERON AND NIOBIUM-93 MAGNETIC RESONANCE STUDY OF NIOBIUM DEUTERIDES

R. G. BARNES, K. P. ROENKER, and H. R. Brooker

Sonderdruck Zeit. Berichte der Bunsen-Gesellschaft für physikalische Chemie (früher Zeitschrift für Elektrochemie) 80: 876 (1976)

Abstract--Niobium deuterides in the composition range $\text{NbD}_{0.55}$ - $\text{NbD}_{0.88}$ were investigated by means of deuteron and ^{93}Nb magnetic resonance over the temperature range 4.2-420 K. The β - α transition, in the temperature range 340-415 K for these compounds, is sharply defined by the extinction of the deuteron quadrupole interaction as well as by the appearance of the central component of the ^{93}Nb spectrum when the cubic α phase is formed. These results are discussed in relation to other determinations of the β - α transition temperature. No other significant changes in the deuteron magnetic resonance spectrum are observed, down to 4.2 K, at which temperature the quadrupole coupling constants are essentially equal, with an average value, $e^2 qQ/h = 33.0$ kHz. The temperature dependent behavior of the ^{93}Nb resonance spectrum indicates that the boundary between the $\alpha + \beta$ and β regions of the Nb-H(D)

phase diagram must pass between the compositions $\text{NbD}_{0.78}$ and $\text{NbD}_{0.82}$ at 300 K. The NMR observations do not furnish positive support for the occurrence of the ξ and ϵ phases nor for the occurrence of the cubic γ phase, but they are not incompatible with the occurrence of these phases. These observations may reflect an intrinsic insensitivity of the deuteron quadrupole interaction to long range ordering of the deuterium in the lattice. Measurements of the ^{93}Nb Knight shift are in close agreement with the shifts obtained in Nb-Mo and Nb-Tc alloys, and suggest that up to this relatively high deuterium content ($\text{D/Nb} = 0.88$) the deuterium continues to yield its electron to the conduction band of the metal.

TEMPERATURE DEPENDENCE OF THE ELECTRIC FIELD GRADIENT IN A QUASI-TWO-DIMENSIONAL METAL: NbSe_2

D. R. TORGESON and F. BORSA

Phys. Rev. Lett. 37: 956 (1976)

Abstract--The ^{93}Nb nuclear-quadrupole-resonance frequencies have been measured as a function of temperature in 2H-NbSe_2 between 38 and 376 K. A nearly linear behavior $\underline{\nu_Q} = \underline{a} - \underline{bT}$ is observed between 77 and 376 K in contrast to an approximate $\underline{\nu_Q}(0)(1 - \alpha T^{3/2})$ dependence found in most noncubic metals over the same temperature range. Using a variation of Jena's theoretical treatment of the temperature dependence of $\underline{\nu_Q}$ in noncubic metals, with the consideration that NbSe_2 is a quasi-two-dimensional structure, we present an explanation of the nearly linear dependence of $\underline{\nu_Q}$ on $\underline{T}$ in NbSe_2 .

EXTREMELY FAST RECOVERY TIME RECEIVER FOR PULSED NMR

D. J. ADDUCI, P. A. HORNING and D. R. TORGESON

Rev. Sci. Instrum. 47: 1503 (1976)

Abstract--A radio-frequency receiver-amplifier for pulsed nuclear magnetic resonance applications is described. This amplifier has a voltage

gain of 2000 and a bandwidth of 5–115 MHz and consists of three identical stages having nonsaturating overload characteristics. Each individual stage recovers within a time of 1 nsec following a 20 dBm overload. The blocking effect of capacitive interstage coupling following rf pulses has been essentially eliminated using series-tuned broad bandwidth resonant circuits between stages. Measured receiver recovery times range from 250 nsec for short (400 nsec) transmitter pulses to 2.0 μ sec for long (75 μ sec) pulses. The effective receiver input noise voltage measured following phase-sensitive detection and at the output of a video amplifier having a bandwidth of 320 kHz was 1.2 μ Z.

ENHANCEMENT OF THE B^{11} NUCLEAR RELAXATION IN CrB_2 NEAR THE ANTIFERROMAGNETIC TRANSITION

F. BORSA and R. G. LECANDER
Solid State Comm. 20: 389 (1976)

Abstract--Measurements of B^{11} nuclear spin-lattice relaxation as a function of temperature in the itinerant antiferromagnet CrB_2 are reported. T_1^{-1} shows a divergent behavior near T_N and it approaches a constant value well above T_N . The results are compared with the different theoretical predictions of Moriya and Ueda obtained either from the RPA or from the re-normalized spin fluctuation approach.

III. SUPERCONDUCTIVITY

SPECIFIC HEAT OF COMPOSITE SUPERCONDUCTORS IN THE PROXIMITY-EFFECT REGIME

A. J. BEVOLO, E. D. GIBSON, J. D. VERHOEVEN and D. K. FINNEMORE
Phys. Rev. B 14: 114 (1976)

Abstract--The specific heat of a series of Pb-Cd laminar composites with layer spacings ranging from 1000 to 85000 Å has been measured in order

to study the superconducting proximity effect in bulk material. The jump in specific heat at the transition temperature is very sensitive to the spatial dependence of the superconducting order parameter and these measurements provide an estimate of this spatial distribution. Results show that the fourth moment of the order parameter is approximately 10% larger than the square of the second moment. The presence of the interleaved nonmagnetic normal-metal layers is not very detrimental to the superconductivity.

PRESSURE DEPENDENCE OF THE SUPERCONDUCTING TRANSITION TEMPERATURE IN ALKALI TUNGSTEN BRONZES

D. BLOOM, H. R. SHANKS, J. BARNES, K. D. McKee, J. E. OSTENSON, and D. K. FINNEMORE

J. Low Temp. Phys. 23: 743 (1976)

Abstract--The superconducting transition temperatures have been measured for the tetragonal I phase of $\text{Na}_{0.23}\text{WO}_3$, the hexagonal phase of $\text{K}_{0.33}\text{WO}_3$, and the hexagonal phase of $\text{Rb}_{0.33}\text{WO}_3$ for pressures up to 20,000 bar. The slope of the curves is $+1.7 \times 10^{-5}$ K/bar for the sodium bronze, -5.8×10^{-5} K/bar for the potassium bronze, and -1.5×10^{-5} K/bar for the rubidium bronze. A sharp change in slope of the transition temperature vs. pressure curve for the potassium bronze at 4000 bar may indicate a phase change.

ELECTRON-PHONON INTERACTION NEAR A NORMAL METAL-SUPER-CONDUCTOR BOUNDARY

J. R. TOPLICAR and D. K. FINNEMORE

Solid State Comm. 19: 859 (1976)

Abstract--Electron tunneling has been used to study the electron-phonon interaction in Pb-Cd proximity effect samples by injecting electrons into the Pb side. For Pb thicknesses ranging from 950 to 330 Å, the phonon structure occurs at the same energy as bulk Pb and the magnitude of the

structure scales as $\frac{T}{T_c}^2$. The shape of the phonon spectral function, $\alpha^2 F(\omega)$, remains essentially unchanged even though $\frac{T}{T_c}$ has been depressed by 35%.

IV. THERMODYNAMIC AND TRANSPORT PROPERTIES OF SOLIDS

THE MELTING CURVE OF HELIUM FROM 4 TO 25 K

J. K. KRAUSE and C. A. SWENSON

Cryogenics p. 413 (1976)

Abstract--New data for the melting curve of He^4 for temperatures between 4 and 25 K agree with earlier results by Mills and Grilly and by Crawford and Daniels, but disagree with the relationship given by Glassford and Smith who carried out equation of state studies on fluid and solid He^4 . The reasons for the disagreement are not clear, but can be interpreted in terms of temperature scale inaccuracies which could have influenced all of their results.

OXIDATION STATE OF TUNGSTEN IN THE Na_xWO_3 BRONZES

G. K. Wertheim, M. Campagna, J.-N. Chazalviel and H. R. SHANKS

Chem. Phys. Lett. 44: 50 (1976)

Abstract--X-ray photoemission spectra of W4f electrons in vacuum-cleaved cubic Na_xWO_3 covering the entire composition range give no evidence for the existence of multiple W valence states in the bulk. Strong oxidation effects are observed in air exposed surfaces.

MOLAR HEAT CAPACITY OF GeTe, SnTe, AND PbTe FROM 0.9 TO 60 K

A. J. BEVOLO, H. R. SHANKS and D. E. ECKELS

Phys. Rev. B 13: 3523 (1976)

Abstract--The molar heat capacity of GeTe, SnTe, and PbTe have been measured by the heat-pulse method from 0.9 to 60 K. No conclusive

evidence was found for the effect of the soft TO phonon modes known to be present in these materials. An anomalous excess heat capacity previously reported near 3 K for GeTe was not confirmed. A detailed comparison of the calorimetric $\Theta_D(T)$ and that calculated from the phonon dispersion curves as measured by inelastic neutron scattering has been made for SnTe and PbTe, with the result that the lattice-dynamical model for PbTe has been verified but a minor refinement is indicated for SnTe. An attempt to explain an anomalous heat capacity for PbTe near 2 K based on the soft TO modes was unsuccessful and the effect remains unexplained. No superconductivity was found in PbTe above 0.9 K.

SURFACE AND ELECTROCATALYTIC PROPERTIES OF TUNGSTEN BRONZES

M. F. WEBER and H. R. SHANKS

Electrocatalysis on Non-Metallic Surfaces, Proceedings of Workshop held at NBS, Gaithersburg, Md., December 9-12, 1975. (November 1976) pp. 297-303

Abstract--Tafel plots have been obtained for the oxygen reaction in acid solution on several alkali tungsten bronzes having different crystal structures. Platinum doped sodium tungsten bronze crystals were studied and the results compared with those of platinum free crystals of the same composition. In both cases sodium tungsten bronzes were found to be poor electrocatalysts for the cathodic reduction of oxygen. Similar results are reported for other alkali tungsten bronzes and for tungsten trioxide. Anodic treatment of the crystals affected the electrocatalytic activity of only the sodium tungsten bronze and the effect was a negative one. Cyclic voltammetry was employed to study the effects of the anodic treatment which created a sodium depletion layer on the sodium tungsten bronze surface. The existence

and depth of the sodium depletion layer was determined by an Auger Electron Spectroscopy depth profile.

V. OPTICAL AND SPECTROSCOPIC PROPERTIES OF SOLIDS AND LIQUIDS

MODULATION SPECTROSCOPY AT NON NORMAL INCIDENCE WITH EMPHASIS ON THE VACUUM-UV SPECTRAL REGION

D. E. Aspnes, C. G. OLSON and D. W. LYNCH
J. Appl. Phys. 47: 602 (1976)

Abstract--Expressions are given to analyze modulation spectra taken at non-normal incidence. These expressions are used to determine the optimum angle of incidence to maximize the signal-to-noise ratio. Significant improvements are shown to be obtained in the vacuum-uv spectral region by making measurements at relatively large angles of incidence. We apply these expressions to evaluate the field-induced change in the dielectric function for the 20.5-21.0-eV core-level doublet in GaP from Schottky-barrier electroreflectance data. The line shape obtained is consistent with that of a field-modulated $\underline{M}_0$ critical point modified by a Coulomb attraction between the core hole and the excited electron.

THERMOREFLECTANCE OF LiF BETWEEN 12 AND 30 eV

M. PIACENTINI, D. W. LYNCH and C. G. OLSON
Phys. Rev. B 13: 5530 (1976)

Abstract--The thermorefectance spectrum of LiF between 12 and 30 eV was measured and several of the structures interpreted. The absorption-edge region is interpreted in terms of a Wannier exciton series converging to the fundamental band gap $\Gamma_{15} \rightarrow \Gamma_1$. Structure associated directly with the

band gap is not manifest, so the $\Gamma_{15}-\Gamma_1$ energy is determined indirectly to be 14.2 ± 0.2 eV. The $n = 1$ exciton state generates the first strong structure in $\Delta\bar{\epsilon}$ and we suggest that the exciton-phonon interaction, along with a central-cell correction, can give a significant contribution to its binding energy. Structures at higher energy have been associated with the interband transitions $\underline{L}_3' \rightarrow \underline{L}_1$ and $\underline{L}_2' \rightarrow \underline{L}_1$ between the crystal-field-split valence band at $\underline{L}$ and the lower conduction band. The strong electron-hole interaction modifies the expected line shape and a hyperbolic exciton, associated with the transitions at $\underline{L}$, may exist as an antiresonance in the continuum. A strong feature at 22.2 eV in $\Delta\bar{\epsilon}$ is associated with excitonic transitions at $\underline{X}$ involving the second $\underline{d}$ -like conduction band. The corresponding peak at 26.4 eV in $\Delta[\text{Im}(-1/\bar{\epsilon})]$ overlaps the "valence-band" plasmon at 24.6 eV. No evidence for double excitations is found around 25 eV in either $\Delta\bar{\epsilon}$ or $\Delta[\text{Im}(-1/\bar{\epsilon})]$. The $\Delta[\text{Im}(-1/\bar{\epsilon})]$ spectrum shows for the first time which structures in the energy-loss function are generated by longitudinal excitons and which by plasmons.

SOFT-X-RAY APPEARANCE POTENTIAL SPECTRA OF La AND Ce FROM 0 TO 1400 eV

R. J. SMITH, M. PIACENTINI, J. L. WOLF, and D. W. LYNCH
Phys. Rev. B 14: 3419 (1976)

Abstract--The soft-x-ray appearance potential spectra were measured for La and Ce in the 0-1400-eV range. The $3\underline{d}$ and $4\underline{d}$ spectra exhibited prominent structure, which is discussed along with x-ray absorption and emission data. The excited electron and the core hole interact strongly, and there is evidence for additional interaction with the projectile electron. The two-density-of-states model of Wendin seems promising for explaining

the spectra, but it must be extended to allow for the interaction of the projectile electron with the excited atom. The effects of oxidation are described.

THERMOREFLECTANCE OF V, Nb, AND PARAMAGNETIC Cr

J. H. WEAVER, D. W. LYNCH, C. H. CULP and R. Rosei

Phys. Rev. B 14: 459 (1976)

Abstract--Thermoreflectance measurements of V, Nb, and Cr films were performed near 80 and 340 K to investigate the electronic properties of these metals. The thermoreflectance spectra $\Delta R/R$ were Kramers-Kronig analyzed to determine the temperature dependence of the dielectric functions. The results were compared with previous derivative measurements of Mo and with static measurements of the optical reflectance of the bcc metals. Interpretation of the structures was guided by recent band calculations. It was shown that the observed features reflect the behavior of large volumes of the Brillouin zone rather than well-defined singularities.

ELECTROABSORPTION OF EXCITONS IN f.c.c. TlBr AND TlCl

J. F. McCLELLAND and D. W. LYNCH

Solid State Comm. 20: 265 (1976)

Abstract--The exciton binding energy, band gap, and static dielectric constant were obtained from electromodulation measurements on the face-centered cubic (NaCl structure) phase of TlBr. An unusual electroabsorption structure has been observed in TlBr and TlCl for features which have no established assignment.

TEMPERATURE COEFFICIENTS OF ENERGY SEPARATIONS BETWEEN Ga 3d CORE LEVELS AND sp^3 VALENCE-CONDUCTION BANDS IN GaP

D. E. Aspnes, C. G. OLSON and D. W. LYNCH

Phys. Rev. Lett. 36: 1563 (1976)

Abstract--The measured temperature coefficients of the energy separations between the Ga 3d core levels and the top (Γ_8^V) and bottom

(X_6^C) of the sp^3 valence and conduction bands in GaP between 110 K and 295 K are $(+ 1.0 \pm 0.5) \times 10^{-4} \text{ eV K}^{-1}$ and $(-2.4 \pm 0.5) \times 10^{-4} \text{ eV K}^{-1}$, respectively. They are described within experimental accuracy by the Debye-Waller, hydrostatic, self-energy, and spatially averaged screened-ion core potential interactions of the sp^3 bands alone. No significant core-level contribution is observed.

ORDERING AND ABSOLUTE ENERGIES OF THE L_6^C AND X_6^C CONDUCTION BAND MINIMA IN GaAs

D. E. Aspnes, C. G. OLSON and D. W. LYNCH
Phys. Rev. Lett. 37: 766 (1976)

Abstract--Resolved critical point structures in Schottky-barrier electroreflectance spectra of Ga $3d^V$ - sp^3 conduction band transitions in the 20-22-eV range provide a direct proof that the L_6^C equivalent minima lie approximately $170 \pm 30 \text{ meV}$ below the X_6^C minima in GaAs. This ordering, opposite to that assumed and apparently supported by previous experiments, is in fact consistent with these experiments and provides natural explanations for many formerly puzzling features of GaAs.

OPTICAL ABSORPTION IN THE $4d$ TRANSITION METALS FROM 20 TO 250 eV

J. H. WEAVER and C. G. OLSON
Phys. Rev. B 14: 3251 (1976)

Abstract--The optical absorption of Y, Zr, Nb, Mo, Rh, Pd, Hf, and W has been measured between 20 and 250 eV using synchrotron radiation from the Tantalus I electron storage ring. The samples were thin, self-supporting films, and transmission measurements were performed at normal incidence. The results were compared with our results from previous reflectivity measurements in the range of overlap (20-40 eV), as well as

with electron-energy-loss measurements where available. The data were interpreted in terms of largely atomiclike transitions of the $4\bar{p}$ -to- $4\bar{d}$ type. Arguments were presented to support this interpretation, and analogies were drawn to the higher-energy $4\bar{d}$ - $4\bar{f}$ transitions in the rare earths. Structures were observed on the low-energy side of the onset which were interpreted in terms of the spin-orbit splitting of the initial $4\bar{p}_{1/2}$ and $4\bar{p}_{3/2}$ states. The broadening of the $\bar{p}$ - $\bar{d}$ structure was interpreted qualitatively in terms of multiplet splitting and autoionization processes. At higher energy, structures related to $3\bar{d}$ transitions were observed.

LINE SHAPE AND SYMMETRY ANALYSIS OF CORE-LEVEL ELECTRO-REFLECTANCE SPECTRA OF GaP

D. E. Aspnes, C. G. OLSON and D. W. LYNCH
Phys. Rev. B 14: 2534 (1976)

Abstract--No dependence of electroreflectance line shapes upon polarization direction or crystal orientation is found for any core-level electroreflectance structure from the Ga $3\bar{d}_{5/2}^V$ core levels to the conduction bands in GaP. Matrix-element effects that are responsible for anisotropy in $\bar{sp}^3$ valence-conduction-band electroreflectance spectra appear to be too weak to be detected in core-level spectra. The result may be general. The field-induced modulation line shape, $\Delta\epsilon_1$, for the Ga $3\bar{d}_{3/2, 5/2}^V - \bar{X}_{6C}^C$ critical points is obtained from the dependence of the spectra and the generalized Seraphin coefficients upon angle of incidence. The line shape is further analyzed to obtain the $\Delta\epsilon_1$ spectrum for Ga $3\bar{d}_{5/2}^V - \bar{X}_{6C}^C$ alone. This procedure yields a spin-orbit splitting $\Delta_{3\bar{d}} = 0.43 \pm 0.02$ eV. A weighting of 0.65 ± 0.05 is also obtained for the $\bar{j} = 3/2$ band relative to the $\bar{j} = 5/2$ band. This is in good agreement with the 4:6 ratio expected on $\bar{d}$ -band occupancy, showing that the

matrix elements are also independent of $\underline{j}$. The line shape of $\Delta\epsilon_{\underline{j}}$ is in good agreement with that predicted by the lifetime-broadened, Coulomb-enhanced Franz-Keldysh theory given by Blossey. The line shape shows a broadening of 160 meV for this transition, and a momentum matrix element about 1/3 as large as that characteristic of $\underline{sp}^3$ valence-conduction-band transitions.

ELECTROREFLECTANCE OF GaSb FROM 0.6 TO 26 eV

D. E. Aspnes, C. G. OLSON and D. W. LYNCH

Phys. Rev. B 14: 4450 (1976)

Abstract--Schottky barrier electroreflectance spectra are reported for GaSb from 0.6 to 26 eV. Accurate energies are determined for a number of critical points between the $\underline{sp}^3$ and Ga-3d valence bands and the conduction bands. The energy of $\underline{X}_{\underline{7}}^{\underline{V}}$ is shown to lie at least 3 eV below $\Gamma_{\underline{8}}^{\underline{V}}$. This is below the value obtained from local pseudopotential calculations and the x-ray photoemission assignments, but follows a trend previously established by nonlocal pseudopotential calculations for Ge and GaAs. The Ga 3d- $\underline{X}_{\underline{6}}^{\underline{C}}$ exciton binding energy is of the order of 100 meV.

SINGLE CRYSTAL RESISTIVITY OF ERBIUM AND Er-Lu ALLOYS BETWEEN 2 AND 300 K

F. H. SPEDDING, B. J. BEAUDRY and W. D. CRESS

Revue de Chimie minérale 13: 62 (1976)

For abstract see Structure of Materials page 19.

THEORETICAL RESEARCH

I. OPTICAL AND SURFACE PHYSICS

SUM RULE FOR THE POLARIZABILITY OF SMALL PARTICLES

R. FUCHS and S. H. LIU

Phys. Rev. B 14: 5521 (1976)

Abstract--A sum rule is derived which is useful for verifying the accuracy of calculated optical properties of arbitrarily shaped particles or powders.

DISPERSION RELATION FOR THE 3.8 eV VOLUME PLASMON OF SILVER

P. Zacharias and K. L. KLIEWER

Solid State Comm. 18: 23 (1976)

Abstract--The dispersion curve of the 3.8 eV volume plasmon of Ag has been obtained by electron energy loss measurements for wave vectors $\underline{q}$ in the range $0.1 \leq \underline{q} \leq 0.35 \text{ \AA}^{-1}$. Results from the low- $\underline{q}$ end of this range match well with the optical results of Lindau and Nilsson. The curve can be described by a dispersion constant $\underline{a} = 0.8 \pm 0.1$ and the intensity of the loss goes like $\underline{I} \sim \underline{q}^{-2.9 \pm 0.4}$. A simple model for the longitudinal dielectric function yields results in good agreement with the experimental conclust.

SURFACE PHOTOEFFECT FOR METALS

K. L. KLIEWER

Phys. Rev. B 14: 1412 (1976)

Abstract--A nonlocal theory for the surface photoeffect produced in metals by vacuum ultraviolet radiation is presented. Using a simple electron-gas model, it is shown that $\underline{p}$ -polarized incident light generates, in the surface region, a strongly spatially dependent vector potential having longitudinal

character; it is argued that the photoemission associated with this longitudinal contribution constitutes the surface photoeffect. Various physical features, including the role of the optical constants and the nondirect nature of the electronic transitions involved, are discussed. It is shown that the nonlocal effects are significant over a wide range of frequencies and for systems other than the electron gas.

ASPECTS OF SPATIAL DISPERSION IN THE OPTICAL PROPERTIES OF
A VACUUM-DIELECTRIC INTERFACE

DAVID LINTON JOHNSON and PETER R. RIMBEY
Phys. Rev. B 14: 2398 (1976)

Abstract--We have examined the relationship between the polarizability for a two-phase (vacuum-dielectric) system and the use of additional boundary conditions and the like, as regards the response of systems exhibiting spatial dispersion. As a consequence we are able to derive information about induced-charge and current densities and the continuity of the field quantities across the interface. It is shown that it is not possible to resonantly excite longitudinal bulk modes with incident light in the formalism of Rimbey-Mahan. We have derived sum rules in wave-vector space on bulk polaritons in homogeneous isotropic systems. In the case of nonhomogeneous perfect crystals in which the bulk response is described by the matrix $\vec{\epsilon}(\vec{Q}, \vec{Q}')$, we have solved formally for the surface impedance in terms of an assumed arbitrary $\vec{\epsilon}(\vec{Q}, \vec{Q}')$, by means of an extension of the Fuchs-Kliwer formalism.

II. SUPERCONDUCTIVITY

ac PERMEABILITY OF DEFECT-FREE TYPE-II SUPERCONDUCTORS

JOHN R. CLEM, H. R. Kerchner and S. T. Sekula

Phys. Rev. B 14: 1893 (1976)

Abstract--A theoretical and experimental study is presented of ac losses in the mixed state of type-II superconductors when viscous damping dominates flux line motion. The theory describes the ac response of a cylindrical superconductor in the mixed state in a dc magnetic field H and a superposed parallel ac field of arbitrary frequency. The complex ac permeability is found to be related to the flux-flow resistivity $\rho_f(B)$, the differential permeability $\mu'(B) = dB/dH$, the frequency, and the sample radius. Measurements were made of the ac permeability in the frequency range 45-1000 Hz of two NbTa alloys which were prepared to minimize bulk pinning and surface losses. Values of $\rho_f(B)$ and $\mu'(B)$ derived from the measurements agree qualitatively with the model, but $\rho_f(B)$ shows a weak frequency dependence that may arise from the presence of remnant nonviscous losses.

FLUX-FLOW VOLTAGES DURING GUIDED FLUX COLLAPSE FROM HOLLOW SUPERCONDUCTING CYLINDERS

S. M. Khanna, JOHN R. CLEM and M. A. R. LeBlanc

Phys. Rev. B 14: 3898 (1976)

Abstract--Voltages across diametrically opposite contact pairs on the outer surface of superconducting Nb tubes are found to depend dramatically upon the spatial configuration of the voltage measuring leads relative to the positions of the moving magnetic flux lines. Experiments have been conducted to study these voltages for different wall thicknesses and for a variety of arrangements of the leads when flux in the hole and the wall of the Nb tube is

made to exit or enter, completely or partially, by applying heat at a narrow strip along its length. The basic concepts of the origin of flux-flow voltages in superconductors are discussed and the importance of the measuring-circuit configuration is stressed. Using the critical-state concept, a model for the change of flux and the resulting electric fields in the Nb tube on application of a heat pulse is presented. The resulting time-dependent and time-integrated voltages are calculated and are in excellent quantitative agreement with our present experimental results. These results show that the flux-flow voltages across two contact points on a superconductor arise from (i) the generation of an induced electric field over a chosen path in the superconductor between the contact points and (ii) a change of magnetic flux through the surface bounded by the measuring leads and the chosen path in the superconductor. Furthermore, the movement of vortex-line segments deep within the superconductor makes no contribution to the measured signal. Use of the flux-flow signals in the study of the dynamics of vortex motion during flux jumps in hollow superconducting tubes is discussed.

ON THE ESTABLISHMENT OF FORCE-FREE CONFIGURATIONS IN TYPE-II SUPERCONDUCTORS

JOHN R. CLEM

Phys. Lett. 59A: 401 (1976)

Abstract--The establishment of helical electrical current and magnetic flux density distributions in cylindrical type-II superconductors is discussed. For the force-free case, a simple relation is shown to connect the local magnetic field and the vortex pitch angle.

III. MAGNETIC AND ELECTRONIC PROPERTIES OF SOLIDS

INDUCED MAGNETIC FORM FACTOR OF CHROMIUM

K. H. OH, B. N. HARMON, S. H. LIU and S. K. SINHA
Phys. Rev. B 14: 1283 (1976)

Abstract--Expressions in terms of Bloch wave functions are derived for the induced nondiagonal magnetic susceptibility $\chi(\vec{G}, 0)$. The expressions for the important contributions are shown to reduce in the tight-binding limit to the usual Pauli spin, Van Vleck orbital, and core diamagnetic terms. Each of these contributions was evaluated for Cr using augmented-plane-wave energy bands and wave functions. The results are in good agreement with the recent measurement of the induced magnetic form factor by Stassis, Kline, and Sinha if an exchange enhancement factor of 2.53 is assumed for the spin contribution. The calculated orbital form factor is isotropic and is essentially identical to the free-ion orbital form factor of Freeman and Watson. The limitations and reasons for the success of the free-ion model are discussed.

COMMENT ON de HAAS-van ALPHEN MEASUREMENTS IN GADOLINIUM

J. E. Schirber, F. A. SCHMIDT, B. N. HARMON and D. D. Koelling
Phys. Rev. Lett. 36: 448 (1976)

Abstract--Fermi-surface cross sections for field along principal symmetry directions for Gd are presented which are in serious disagreement with those of previous investigators. This disagreement stems from the use of an incorrect value for the saturation magnetization. The new frequency values are compared with the results of a relativistic augmented-plane-wave band calculation.

PHONON ANOMALIES IN d-BAND METALS AND THEIR RELATIONSHIP
TO SUPERCONDUCTIVITY

S.K. SINHA and B. N. HARMON

Superconductivity in d- and f-Band Metals, ed. D. H. Douglass (New York: Plenum Publishing Corp., 1976) pp. 269-296

Abstract--Many high T_c d- and f-band superconductors exhibit actual or incipient lattice instabilities as evidenced by structural transitions or anomalous dips in their phonon dispersion curves. We present a theory demonstrating that the dips and high T_c 's in these materials are likely manifestations of the characteristic response (screening) by d-electrons near the Fermi level. In materials with a relatively large density of localized states at the Fermi level there is a tendency towards a collective electronic instability characterized by a periodic charge redistribution. However a charge density wave does not form because these charge fluctuations are strongly coupled to the lattice giving rise to anomalies in the phonon spectrum and in some cases eventually driving the lattice into a structural transformation. By including relaxation of the fluctuations the central peak observed by neutron diffraction in many of these materials can also be understood. In regions of $\vec{q}$ -space where such incipient electronic instabilities are present there is lessened screening or relative enhancement of the electron-phonon matrix elements - giving rise to larger λ 's and thus greater T_c 's. The details of the theory are sketched and the physical ideas explained. A simplified application of the theory to Nb and NbC shows that the positions of the dips are readily accounted for and that the size of depth of these anomalies is very sensitive to the density of states at E_F . The relationship to other work is discussed.

CALCULATION OF THE ELECTRON-PHONON SPECTRAL FUNCTION OF NIOBIUM

B. N. HARMON and S. K.

Superconductivity in d- and f-Band Metals, ed. D. H. Douglass (New York: Plenum Publishing Corp., 1976) pp. 391-412

Abstract--The electron-phonon spectral distribution function, $\alpha^2 F(\omega)$, has been calculated for niobium using the wavefunctions and potential from a self-consistent APW calculation. The results are compared with recent tunneling experiments, and indicate the great significance of screening. An omission in the formulas of Gaspari and Gyorffy is pointed out.

NO GIANT TWO-ION ANISOTROPY IN THE HEAVY-RARE-EARTH METALS PER-ANKER LINDGARD

Phys. Rev. Lett. 36: 385 (1976)

Abstract--A new Bose-operator expansion of tensor operators is applied to the heavy-rare-earth metals. The Er data for the cone phase have been analyzed successfully with single-ion anisotropy and isotropic exchange interaction. The Tb data can be understood on the same basis. The previously found large two-ion anisotropy was due to an inadequate treatment of the large single-ion anisotropy leading to an incorrect expression for the spin-wave energy.

ELECTRONIC STRUCTURE, FIELD-INDUCED MAGNETIZATION DENSITY AND NEUTRON MAGNETIC FORM FACTOR OF PALLADIUM

T. J. Watson-Yang, B. N. HARMON and A. J. Freeman
J. Magnetism & Magnetic Materials 2: 334 (1976)

Abstract--The magnetic field induced magnetization density and neutron magnetic form factor of Pd metal is obtained from an ab initio APW energy band study of its electronic structure and properties. The magnetization consists of the spin density calculated for states on the Fermi surface and a much smaller orbital contribution. The solid state wavefunctions are

found to yield a spatial localization of the spin density which is greater than that of the very contracted Hartree-Fock density of the free Pd^{2+} ion. The theoretical magnetic form factor, which is dominated by the contribution of the fifth band, is found to be in excellent agreement with the measurements of Cable, Wollan, Felcher, Brun and Hornfeldt.

KONDO SCATTERING IN A PURE METAL-- β CERIUM: II. THEORETICAL
S. H. LIU, P. BURGARDT, K. A. GSCHNEIDNER, Jr. and S. LEGVOLD
J. Phys. F: Metal Phys. 6: L55 (1976)

Abstract--This letter contains a detailed explanation of the anomalous electrical resistivity of β cerium.

MAGNETIC EXCITATIONS ABOVE THE CRITICAL TEMPERATURE
S. H. LIU
Phys. Rev. B 13: 2979 (1976)

Abstract--We present a simple but physically motivated approximation scheme for the dynamical spin correlation function of the Heisenberg model above the critical temperature. Built upon the spin-diffusion theory, it describes the short-wavelength and high-frequency excitations as magnonlike modes which exist within clusters of highly correlated spins. The modes are damped by both the finite size and the finite lifetime of the clusters. The agreement between the theory and the neutron scattering data on a variety of systems is reasonably good.

QUASISPIN MODEL OF ITINERANT MAGNETISM
S. H. LIU
Phys. Rev. B 13: 3902 (1976)

Abstract--The problem of spin waves in itinerant ferromagnets and antiferromagnets is discussed from the band-theory point of view. In the ground state, the energy bands are spin split and there is a spin-density

cloud around each ion site. When a spin wave is excited, we postulate that the spin cloud of each ion precesses as a rigid unit, i.e., a quasispin. This gives rise to a modulation of the effective exchange potential, and the difference between the modulated potential and the ground-state exchange potential has the form of the s-d interaction. Here the s part includes all the conduction electrons and the d part arises from the precession of the quasispins. The magnon energy, electron band splitting, and the magnon-magnon interaction are discussed. In every case the agreement between the result and the experiment is as good as or better than the existing theories.

CONCENTRATION-DEPENDENT KOHN EFFECT IN CUBIC TUNGSTEN BRONZES

W. A. KAMITAKAHARA, B. N. HARMON, J. G. TAYLOR, L. KOPP,
H. R. SHANKS and J. Rath
Phys. Rev. Lett. 36: 1393 (1976)

Abstract--Inelastic neutron scattering measurements on single crystals of cubic Na_xWO_3 reveal a large concentration-dependent Kohn anomaly in the $[100]$ longitudinal acoustic-phonon dispersion curve. The results demonstrate the two-dimensional character of the Fermi surface, support the rigid-band model for $0.56 < x < 0.83$, and conflict with the percolation model which has just recently been proposed to explain the transport properties of the tungsten bronzes.

Materials Chemistry

CHEMICAL STRUCTURE

I. X-RAY AND NEUTRON CRYSTALLOGRAPHY

CRYSTAL STRUCTURE STUDIES OF TETRAGONAL SODIUM TUNGSTEN BRONZES, Na_xWO_3 , I. $\text{Na}_{0.33}\text{WO}_3$ AND $\text{Na}_{0.48}\text{WO}_3$

FUSAO TAKUSAGAWA and ROBERT A. JACOBSON
J. Solid State Chem. 18: 163 (1976)

Abstract--The crystal structures of two sodium tungsten bronzes, $\text{Na}_{0.33}\text{WO}_3$ and $\text{Na}_{0.48}\text{WO}_3$, have been determined by three-dimensional single-crystal x-ray analysis. They were found to crystallize in the tetragonal space groups $\overline{P}4_2m$ ($a = 12.097$, $c = 3.754$ Å, $Z = 10$) and $\overline{P}4/mbm$ ($a = 12.150$, $c = 3.769$ Å, $Z = 10$), respectively. The structures were solved by standard Patterson and Fourier techniques and refined by full-matrix least-squares to final conventional discrepancy indices of 8.9% for $\text{Na}_{0.33}\text{WO}_3$ and 8.4% for $\text{Na}_{0.48}\text{WO}_3$. In general, the oxygen atoms were found to be either twofold or fourfold disordered, suggesting that the WO_6 octahedra do not have axes exactly aligned parallel to the crystallographic c -axis. The structure found can be viewed as a composite of two kinds of domain structures. These domain structures would require a doubling of the c -axis along with selection of new a - and b -axes along the $[110]$ and $[\overline{1}10]$ directions. There exist pentagonal and tetragonal sites in both these sodium tungsten bronzes for sodium atoms occupancy. In Na_xWO_3 , $x = 0.48$, all the pentagonal sites are filled and 40% of the smaller tetragonal sites are also occupied.

As $\underline{x}$ decreases to 0.33 though, only the pentagonal sites are occupied. A relation between the $\underline{x}$ value and the $\text{Na}_{\underline{x}}\text{WO}_3$ crystal structures is postulated, extrapolating from the results found in these structure determinations.

THE CRYSTAL AND MOLECULAR STRUCTURE OF DIAQUOBIS (2,3-DIHYDROXY-2-METHYLPROPANOATO) COPPER(II)

J. H. MILLER, J. E. POWELL, R. A. JACOBSON and S. KULPRATHIPANJA

Inorg. Chim. Acta 18: 25 (1976)

Abstract--The crystal and molecular structure of diaquobis(2,3-dihydroxy-2-methylpropanoato)copper(II) has been determined by three-dimensional x-ray analysis. The compound crystallizes in the monoclinic space group $\underline{C2/c}$, with $\underline{a} = 5.688 \pm .006 \text{ \AA}$, $\underline{b} = 20.79 \pm .03 \text{ \AA}$, $\underline{c} = 10.569 \pm .016 \text{ \AA}$, $\beta = 94.55 \pm .06^\circ$, and $\underline{Z} = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final discrepancy factor $\underline{R} = .090$ for 860 observed reflections ($\underline{I}_0 > 2\sigma(\underline{I}_0)$). The geometry around the copper is distorted octahedral, with the two waters occupying the axial positions. Both ligands coordinate bidently, forming chelate rings incorporating the 2-hydroxy oxygen. The other hydroxy oxygens are not bound to the copper. There appears to be extensive hydrogen bonding in both the $\underline{a}$ and $\underline{c}$ directions with long contacts in the $\underline{b}$ direction.

THE CRYSTAL STRUCTURE OF 3,7-DIHYDROXY-1,5-BIS(p-BROMO-

PHENYL)OCTAHYDRO-1,5-DIAZOCINE ETHANOL SOLVATE, $\text{C}_{18}\text{H}_{20}\text{Br}_2\text{N}_2\text{O}_2 \cdot \text{C}_2\text{H}_5\text{O}$

Cary Peters, William P. Jensen, James J. Worman, ROBERT A. JACOBSON and David A. Nelson

Cryst. Struct. Comm. 5: 905 (1976)

Abstract--The chemistry of octahydro-1,5-diazocines has been of interest for a number of reasons. The system undergoes a very facile ring

of contraction to yield substituted piperazines. Upon reaction with PBr_3 only two bromomethyl isomers of piperazine can be isolated and these are of the cls configuration. In order to better understand the mechanism of the reaction and the resulting stereochemistry of the products the x-ray structure determination of the title compound was undertaken.

PHENYL TROPYLIUM FLUOROBORATE-TRIPHENYLMETHYL FLUORIDE,
 $\text{C}_{32}\text{H}_{26}\text{BF}_5$

FUSAO TAKUSAGAWA, ROBERT A. JACOBSON, WALTER S. TRAHANOVSKY
 and M. DWIGHT ROBBINS
 Cryst. Struct. Comm. 5: 753 (1976)

Abstract--A standard method for the preparation of tropylium fluoro-
 borates involves hydride ion abstraction from the corresponding cyclohep-
 tatriene by the trityl cation which is prepared from triphenylmethanol and
 fluoroboric acid. This method has been used successfully for the preparation
 of phenyltropylium fluoroborate; however, from one run which we carried out,
 a crystalline material was obtained whose proton NMR spectrum consisted of
 signals from the phenyltropylium ion and additional aromatic protons. In an
 effort to characterize this material, a crystal structure determination of it
 was carried out and it was found to be a mixed crystal of phenyltropylium
 fluoroborate and triphenylmethyl fluoride. An elemental analysis of this
 material was also found to be consistent with this composition: Calcd, for
 $\text{C}_{32}\text{H}_{26}\text{BF}_5$: C, 74.43; H, 5.06. Found: C, 74.41; H, 5.25.

PYRIDINIUM TETRABROMOANTIMONATE(III) $\text{C}_5\text{H}_5\text{N}^+\text{Sb}^{\text{III}}\text{Br}_4^-$

PATRICK W. DeHAVEN and ROBERT A. JACOBSON
 Cryst. Struct. Comm. 5: 31 (1976)

Abstract--As part of a series of investigations of halo-coordinated
 antimony compounds being performed in this laboratory, the structure of

pyridinium tetrachloroantimonate(III) was determined and found to have a unique structure in which the SbCl_4^- ion forms an infinite chain via chlorine bridges. A pyridinium-antimony-bromine species of formula $(\text{C}_5\text{H}_5\text{NH})_5^- \text{Sb}_2\text{Br}_9 \cdot (\text{Br})_2$ had been prepared and structurally characterized, but no conclusive structural evidence for an SbBr_4^- moiety has been heretofore presented. A sample of $\text{C}_5\text{H}_5\text{NH Sb}^{\text{III}}\text{Br}_4$ was prepared and kindly supplied to us by Dr. G. G. Long. Recrystallization from acetonitrile yielded pale yellow plate-like crystals. A single plate, 0.18, 0.12, 0.02 mm, was mounted on the end of a glass fiber with Duco cement for structural determination.

A SINGLE-CRYSTAL AUTOMATIC INDEXING PROCEDURE

ROBERT A. JACOBSON

J. Appl. Cryst. 9: 115 (1976)

Abstract--An algorithm has been developed and implemented to determine automatically the indices and other reciprocal-lattice information from the positions of a dozen or so arbitrary reflections on a four-circle diffractometer. Output includes the indices; reduced cell dimensions, and the reduced cell scalars for Bravais lattice determination. Illustrations of the use of the indexing procedure both with the four-circle diffractometer and with precession camera techniques are given. A comparison to some other autoindexing procedures is also given.

STRUCTURE OF $\text{trans-W(CO)}_4(\text{CNC}_6\text{H}_{11})(\text{CS})$ AND A CORRELATION OF $\nu(\text{CS})$ FREQUENCIES WITH C-S BOND DISTANCES IN METAL THIO-CARBONYL COMPLEXES

SCOTT S. WOODARD, ROBERT A. JACOBSON and ROBERT J. ANGELICI
J. Organomet. Chem. 117: C75 (1976)

Abstract--An x-ray structural investigation of $\text{trans-W(CO)}_4(\text{CNC}_6\text{H}_{11})(\text{CS})$ shows that the W-C bond distances to the 3 isoelectronic ligands increase

in the order: $W-CS(1.944\text{\AA}) < W-CO(2.0645\text{\AA}, \text{average}) < W-CNC_6H_{11}^-$
 $(2.158\text{\AA})$. Using data from this molecule as well as results from other
 thiocarbonyl complexes reported in the literature, an excellent correlation
 of low $\nu(CS)$ frequencies with long C-S bond distances is observed, a trend
 which supports current bonding theories for thiocarbonyl complexes.

TRIS(NITRATO)TETRAAQUOPRASEODYMIUM(III) DIHYDRATE, $Pr(NO_3)_3 \cdot$
 $(H_2O)_4 \cdot 2H_2O$

CHARLES C. FULLER and ROBERT A. JACOBSON
 Cryst. Struct. Comm. 5: 349 (1976)

Abstract--A crystal and molecular structure determination of this-
 (nitrate)tetraaquopraseodymium(III) dihydrate was initially carried out by
 Volodina, Rumanova, and Belov (1961). This determination was based on
 data gathered using film techniques and no crystallographic discrepancy factor
 or thermal parameters were given. Since we desired more accurate distances
 and angles in order to compare with other rare earth complexes, we decided
 to compare the crystal and molecular structure using a four-circle automated
 diffractometer and counter techniques.

CRYSTAL AND MOLECULAR STRUCTURE OF ORGANOPHOSPHORUS
INSECTICIDES. II. COROXON

MICHAEL R. GIFFKINS and ROBERT A. JACOBSON
 J. Agric. Food Chem. 24: 232 (1976)

Abstract--The detailed molecular structure of Coroxon [O,O-diethyl
O-(3-chloro-4-methyl-2-oxo-(2H)-1-benzopyran-7-yl) phosphate] has been
 determined by single-crystal x-ray diffraction techniques. The space group
 is $P2_1/c$ with $a = 9.305(3)$, $b = 23.114(10)$, and $c = 7.815(2)\text{\AA}$, $\beta = 108.52(3)^\circ$,
 and four molecules in the unit cell. Direct methods yielded an initial struc-
 tural model and subsequent least-squares refinement based on the 1202

observed ($I > 3\sigma_I$) structure factors gave a final agreement factor of 4.0%.

The geometry around the phosphorus atom is distorted from tetrahedral with angles ranging from 100.6 (2) to 116.0 (2)°. A comparison of the three single P-O bonds indicates that the bond to the oxygen of the aryl group is somewhat elongated relative to the others (1.593 (3) vs. 1.551 (4) and 1.554 (4) Å). Distances from the phosphorus to the centers of the two fused rings are 3.93 and 5.80 Å.

CRYSTAL AND MOLECULAR STRUCTURE OF ORGANOPHOSPHORUS INSECTICIDES. 3. AZINPHOS-METHYL

WAYNE J. ROHRBAUGH, ELAINE K. MEYERS, and ROBERT A. JACOBSON
J. Agric. Food Chem. 24: 713 (1976)

Abstract--The crystal and molecular structure of azinphos-methyl (O,O-dimethyl S-(4-oxo-1,2,3-benzotriazin-3-yl)methyl phosphorodithioate), $C_{10}H_{12}N_3O_3PS_2$, has been determined by three-dimensional x-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.084 \pm 0.007$, $b = 15.190 \pm 0.008$, $c = 7.856 \pm 0.003$ Å, and $\beta = 98.39 \pm 0.03^\circ$ with $Z = 4$. Graphite-monochromated MoK α radiation ($\lambda = 0.70954$ Å) was used for measurement of diffraction data at 10°C. The structure was solved via direct methods and refined by a full-matrix least-squares procedure to a final discrepancy index of $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.080$. The phosphorus-(carbonyl carbon) distance corresponding to the anionic-esteratic site separation of acetylcholinesterase is 4.83 (2) Å for azinphos-methyl in the solid state. No appreciable intramolecular interactions which might limit the accommodation of a large range of anionic-esteratic separations were observed.

CRYSTAL AND MOLECULAR STRUCTURE OF ORGANOPHOSPHORUS
INSECTICIDES. 4. BROMOPHOS

RUSSELL G. BAUGHMAN and ROBERT A. JACOBSON

J. Agric. Food Chem. 24: 1036 (1976)

Abstract—The crystal and molecular structure of bromophos (O-(4-bromo-2,5-dichlorophenyl) O, O-dimethyl phosphorothioate, $(\text{H}_3\text{CO})_2\text{P}(\text{S})\text{OC}_6\text{H}_2\text{Cl}_2\text{Br}$, orthorhombic, $\underline{P}2_12_12_1$, $\underline{a} = 7.307(5)$, $\underline{b} = 27.19(3)$, and $\underline{c} = 6.440(4)$ Å, $\underline{Z} = 4$, Mo $K\alpha$ radiation) has been determined by three-dimensional x-ray analysis. The structure was solved by conventional Patterson and Fourier techniques to a final discrepancy index $\underline{R} = 0.048$ for 1217 observed reflections [$\underline{F}_0 > 2.5\sigma(\underline{F}_0)$]. The structure features an intramolecular hydrogen bond which restricts rotation about the phenolic C-O bond, thus giving a very probable in vivo model. The phosphorus-meta hydrogen distance of 5.52 Å falls well within the range of literature values cited for the intramolecular active site-separation distance for acetylcholinesterase (AChE), yet is well outside that for mammalian AChE.

II. METAL-METAL BONDING

HOMOPOLYATOMIC IONS OF THE POST-TRANSITION ELEMENTS--
SYNTHESIS, STRUCTURE, AND BONDING

JOHN D. CORBETT

Chemistry Vol. 21. ed., S. J. Lippard (New York: John Wiley & Sons, 1976) pp. 129-158.

Abstract--A significant number of homopolyatomic or "cluster" ions may now be prepared with the post-transition elements, and all but the most stable example, Hg_2^{2+} , require relatively acidic conditions for stability. The present chapter is concerned principally with those polyatomic cations, for example, Cd_2^{2+} , Bi_9^{5+} , and Te_4^{2+} , which can be obtained as equilibrium phases from acidic melt systems as halometallate salts, mainly with AlCl_4^- .

THE CRYSTAL STRUCTURE OF THULIUM(II) CHLORIDE

TORMOD NATERSTAD and JOHN D. CORBETT

J. Less-Common Metals 46: 291 (1976)

Abstract--An earlier investigation of the TmCl_3 -Tm system revealed an unusually large number of thermal arrests in the approximate region $2.16 > \text{Cl/Tm} \geq 2.04$, which was tentatively explained in terms of a series of at least nine closely-spaced phases. Subsequent x-ray investigation of this phase region included the present study of the structure of TmCl_2 as it is evidently the structural end-member of the series. The dichloride has previously been reported to be isostructural with YbCl_2 (SrI_2 -type) on the basis of powder pattern data, a conclusion which is confirmed in detail by the single-crystal study reported here together with similar data recently reported for YbCl_2 .

CRYSTAL STRUCTURE OF ZIRCONIUM MONOCHLORIDE. A NOVEL PHASE CONTAINING METAL-METAL BONDED SHEETS

DOUGLAS G. ADOLPHSON and JOHN D. CORBETT

Inorg. Chem. 15, 1820 (1976)

Abstract--Monocrystals of ZrCl were obtained by the reaction of $\text{ZrCl}_4(\text{g})$ with a large excess of electropolished Zr in a sealed tantalum tube under a $600\text{--}800^\circ\text{C}$ gradient for 24 days. Integrated diffraction data were secured on an automated diffractometer using $\text{Mo K}\alpha$ radiation. Systematic absences among 203 observed reflections together with tuned diffraction data established a C-centered monoclinic cell with $\underline{a} = 5.943(6)$, $\underline{b} = 3.419(3)$, $\underline{c} = 9.087(18) \text{ \AA}$, $\beta = 102.5(1)^\circ$, $\underline{Z} = 4$. The structure was solved by standard Patterson and Fourier techniques to a conventional residual of 0.080 and $\underline{R}_w = 0.087$. The structure contains homoatomic layers sequenced Cl-Zr-Zr-Cl so as to generate four-layer sheets, the layers and sheets being geometrically

close to cubic close packed along [001]. The result is found to be within experimental error of a higher symmetry trigonal cell ($Z = 6$) with the rhombohedral space group $R\bar{3}m$. The diffraction data were therefore converted, averaged, and refined utilizing 85 independent reflections, half as many positional parameters, and $a = 3.424$ (2), $c = 26.57$ (4) Å to give $R = 0.071$ and $R_w = 0.087$. Distances are not statistically distinguishable in the two refinements; although the rhombohedral description is formally preferred, the real symmetry probably depends appreciably on the crystalline perfection in the [001] direction. Each zirconium atom has three neighbors in the adjacent sheet at 3.09 Å (Pauling bond order of 0.5), six more in the same sheet at 3.42 Å, and three chlorine atoms on the other side at 2.63 Å. Weak chlorine-chlorine interactions between sheets at 3.61 Å contrast with the strong metal-metal binding within the sheets; the former are presumably responsible for the graphitic properties and anisotropic conduction of the compound.

REDUCED HALIDES OF THE RARE EARTH ELEMENTS

JOHN D. CORBETT

Proceedings 12th Rare Earth Research Conference, ed. C. E. Lundin (Denver, Colorado: University of Denver and Denver Research Institute, 1976) Vol. I pp. 396-399.

Abstract--The tremendous diversity in the behavior of the rare earth metal trihalides on reduction is in considerable contrast to the traditional view of great similarity found with many properties of the lanthanide series. Experimentally, formation of reduced phases of other than the easily reduced SmX_3 , EuX_3 and YbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) is best affected in tantalum tubing at elevated temperatures, this container completely avoiding contamination (or even destruction) of the products which occurs in glass through formation of

the very stable silicides and oxides. The nature of the studies and the products formed may be subdivided fairly well into reactions of metal (A) with liquid trihalides forming liquid and solid MX_n phases, $2 \leq n < 3$, with relatively isolated reduced ions, and (B) with gaseous trihalides (or equivalent) at lower MX_3 activity and rate which produce phases MX_m , $1 \leq m < 1.5$ or 2, with extended metal-metal bonding.

STABLE HOMOPOLYATOMIC ANIONS OF THE POST-TRANSITION METALS. "ZINTL IONS". THE SYNTHESIS AND STRUCTURE OF A SALT CONTAINING THE HEPTANTIMONIDE(3-) ANION

DOUGLAS G. ADOLPHSON, JOHN D. CORBETT, and DON J. MERRYMAN
J. Am. Chem. Soc. 98: 7234 (1976)

Abstract--The phenomenon of the formation of homopolyatomic or the so-called Zintl anions on solution of many alloys in liquid ammonia is considered, and a general route to the isolation of stable homopolyatomic anions illustrated in the case of antimony. The dark brown crystalline (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (sodium) heptantimonide(3-), $(C_{18}H_{36}N_2O_6 \cdot Na^+)_3Sb_7^{3-}$, has been prepared from the reaction of a sodium-antimony alloy with $C_{18}H_{36}N_2O_6$ (2,2,2-crypt) in ethylenediamine. Lattice constants $\underline{a} = 23.292$ (7) Å, $\underline{b} = 13.791$ (6) Å, $\underline{c} = 25.355$ (6) Å, and $\beta = 108.56$ (2)° with four molecules per unit cell in space group $\underline{P2}_1/\underline{n}$ were deduced from three-dimensional x-ray data collected from a single crystal of the compound on a four-circle diffractometer using Mo $K\alpha$ radiation. The problem was phased using direct methods. Stepwise full-matrix least-squares refinement of the ten heavy atoms with anisotropic thermal parameters and of the 78 light atoms of the crypts with isotropic temperature factors resulted in converged atomic parameters with $\underline{R} = 0.111$ and $\underline{R}_w$

= 0.134. Three cryptated sodium cations in which the sodium ion occupies the central cavity of the macrobicycle occur together with the Sb_7^{3-} cluster anion, the first example of a well-characterized polyatomic anion for a metallic element. The polyantimony anion exhibits approximate C_{3v} symmetry as an end-capped trigonal prism with the capped face substantially expanded, analogous to the isoelectronic P_4S_3 . Bond distances in the cluster range from 2.693 (4) to 2.880 (4) Å. Possible geometries for several other reported Zintl ions of the group 5 elements are proposed on the basis of known isoelectronic ions or molecules.

III. CHEMISTRY OF HEAVY TRANSITION METALS

A NOVEL HETEROMETALLIC MOLECULE CONSISTING OF A NEW TRIANGULAR TUNGSTEN CLUSTER BRIDGED BY OXOCHROMIUM AND ALKOXY LIGANDS

V. KATOVIC, J. L. TEMPLETON, and R. E. MCCARLEY
J. Am. Chem. Soc. 98: 5705 (1976)

Abstract--The new compound $\text{W}_3(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3\text{O}_3\text{Cr}_3(\text{O}_2\text{CC}(\text{CH}_3)_3)_{12} \cdot 2\text{C}_6\text{H}_4\text{Cl}_2$ has been isolated from the reaction of $\text{W}(\text{CO})_6$, $\text{Cr}(\text{CO})_6$ and pivalic acid in a 1:1:2 ratio, respectively, in refluxing o-dichlorobenzene. The green crystals are paramagnetic, $\mu(\text{mol}) = 6.44$ B.M. (or 3.72 B.M. per Cr atom), determined over the range 77-300 K, and provide a mass spectrum with a set of peaks centered at 2055 characteristic of the molecular ion. An x-ray structure determination shows the crystals are monoclinic, $a = 23.479(10)$, $b = 18.395(9)$, $c = 23.535(9)$ Å, $\beta = 99.59(3)^\circ$, space group $\text{P}2_1/\text{n}$, $Z = 4$. Solution and refinement of all nonhydrogen atoms revealed the molecular unit $\text{W}_3(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3\text{O}_3\text{Cr}_3(\text{O}_2\text{CC}(\text{CH}_3)_3)_{12}$ which consists of a new triangular tungsten cluster ($d(\text{W}-\text{W}, \text{ave.}) = 2.610(1)$ Å) bridged on

each edge by oxo O-atoms ($d(W-O, \text{ave.}) = 1.96 \text{ \AA}$) and over the opposite face by the triply bridging alkoxo O-atom ($d(W-O, \text{ave.}) = 2.13 \text{ \AA}$). Each oxo O-atom is also coordinated to one Cr. The molecule then is multiply inter-linked by the carboxylate ligands which bridge between the W and Cr atoms. An analysis of bonding of the W_3O_{13} cluster group shows tungsten in the average oxidation state 3.33+, and 8 electrons are involved in the W-W bonding.

SOME UNUSUAL DIMERIC AND CLUSTER SPECIES OF THE GROUP VI TRANSITION METALS

R. E. MCCARLEY, J. L. TEMPLETON, T. J. COLBURN, V. KATOVIC and R. J. HOXMEIER

Inorganic Compounds with Unusual Properties, Advances in Chemistry Series No. 150, ed., Bruce King (Washington, D.C.; American Chemical Society, 1976) pp. 318-334

Abstract--Several new compounds of molybdenum and tungsten that have multiple metal-metal bonds are described. It is concluded that the compounds $[Mo_2(O_2CR)_4]I_3$ ($R = C_2H_5$, $C(CH_3)_3$, or C_6H_5), formed by reaction of $Mo_2(O_2CR)_4$ with iodine in noncoordinating solvents, are I_3^- salts of the cations $[Mo_2(O_2CR)_4]^+$ with Mo-Mo bond order of 3.5. The first species containing quadruply bonded tungsten, $MoW(O_2C(CH_3)_3)_4$, was prepared in mixtures with $Mo_2(O_2CR)_4$ with which it is isostructural and isomorphous. The mixtures were separated by iodination in benzene, which provided $[MoW(O_2CC(CH_3)_3)_4]I$ containing the one-electron oxidized cation $[MoW(O_2CC(CH_3)_3)_4]^+$ with Mo-W bond order of 3.5. The compound $[(C_3H_7)_4N]_2W_2Br_9$, prepared by reaction between $[(C_3H_9)_4N]W(CO)_5Br$ and dibromoethane, contains the new confacial bioctahedral anion $W_2Br_9^{2-}$.

$d(W-W) = 2.58(I) A$, and $\mu(\text{exp.}) = 1.72 \text{ BM}$. An unusual mixed halide complex $[(C_4H_9)_4N]_2Mo_4I_{10}Cl$ is also reported.

ENGINEERING CHEMISTRY

I. LIQUID METALS

THE HEAT CAPACITIES AND HEAT CONTENT OF MOLTEN CERIUM BY LEVITATION CALORIMETRY

LYLE K. KUNTZ and RENATO G. BAUTISTA
Met. Trans. B 7B: 107 (1976)

Abstract--A 15 kva, 450 khz radio frequency generator was used to levitate and melt cerium samples ranging in size from 0.4 gms to 1.7 gms. The molten cerium samples were then dropped into a copper block calorimeter contained in isothermal surroundings. The cerium data between 1400 K and 1700 K indicated a nonlinear heat content function as described by the equation:

$$H_T - H_{298.15} = -0.01255 T^2 + 75.305 T - 32,995.401 \text{ J/mol.}$$

The correlation coefficient for the curve fitting process was 0.81. The data between 1700 K and 2500 K indicated a linear heat content function as described by the equation:

$$H_T - H_{298.15} = \{31.616 \pm 0.596\}(T - 1077) + \{38,917.267 \pm 575.049\} \text{ J/mol.}$$

The average percent deviation between this and the experimental values was 0.67. Experimental heat contents were corrected for convection and radiation heat losses during the fall of the sample from the levitation chamber into the calorimeter. The maximum estimated error for the levitation calorimetry work was $\pm 2.5 \text{ pct.}$

LIQUID PRASEODYMIUM HEAT CONTENT BY LEVITATION CALORIMETRY

LAWRENCE A. STRETZ and RENATO G. BAUTISTA

J. Chem. Eng. Data 21: 13 (1976)

Abstract--The high-temperature heat content of liquid praseodymium was measured experimentally by the levitation calorimetry technique. The samples, ranging in size from 0.5 to 1.5 g, were simultaneously levitated and heated by a radiofrequency generator in an argon-helium mixture prior to being dropped into a conventional copper block drop calorimeter. Corrections were made for the convection and radiation losses during the fall of the sample from the levitation chamber into the calorimeter. The praseodymium data, from 1460 to 2289 K, were fitted by the following equation where the indicated errors represent the average deviation of the experimental value from the value predicted by the equation:

$$\frac{H_T}{T} - \frac{H_{298.15}}{298.15} = \{41.57 \pm 0.29\} (T - 1208) + \{41733 \pm 197\} \text{ J/mol.}$$

II. RECOVERY OF METAL VALUES FROM FLY ASH

THE LIME-SINTER PROCESS FOR PRODUCTION OF ALUMINA FROM FLY ASH

K. S. CHOU, W. A. KLEMM, M. J. MURTHA and G. BURNET

Proc. 4th International Ash Utilization Symposium, eds. John H. Faber, Allan W. Babcock and John D. Spencer (ERDA-MERC: Morgantown, West Virginia, 1976) MERC/SP-76/4 pp. 433-449.

Abstract--Fly ash, the product from burning pulverized coal in power plant furnaces, is produced in large quantities. In 1970, the U.S. production was 28 million tons, and it is expected that by 1980 the production will be around 40 million tons. With this large source of essentially waste

material available at convenient locations, near power and transportation, one has the desire to obtain something of value from it.

Fly ash consists essentially of oxides. The oxide present in greatest amount is silica, either free, or combined as silicates and aluminates. The compositions vary, depending on the coal source, but a typical chemical composition of one that we shall designate C-1 is given in Table 1. The oxides of value are alumina and iron oxide.

RECOVERY OF ALUMINA FROM COAL FLY ASH BY HIGH TEMPERATURE CHLORINATION

M. J. MURTHA and G. BURNET

Proc. Iowa Acad. Sci. 83: 125 (1976)

Abstract--Recovery of metals from low value sources will help reduce our national demand for foreign resources. The ash from bituminous type coals contains about 20 percent aluminum oxide and 20 percent iron oxides by weight. Recovery of these metals would provide an alternate source to the ores now used. The iron and aluminum materials in fly ash are recoverable by high temperature chlorination. Passing dry chlorine gas through a bed of nonmagnetic fly ash maintained at 850 to 900°C chlorinates the iron and aluminum constituents forming volatile compounds which are carried from the bed by the exit gas stream. In exploratory runs, 55 per cent of the aluminum has been recovered as aluminum chloride in a nearly silica-free state.

III. EMITTANCE PROPERTIES OF MATERIALS AT HIGH TEMPERATURES

THE NORMAL SPECTRAL EMITTANCE OF YTTRIUM, LANTHANUM, CERIUM, PRASEODYMIUM AND NEODYMIUM ABOVE 1000 K

DORAB N. BARIA, TERRY S. KING and RENATO G. BAUTISTA

Met. Trans. B 7B: 577 (1976)

Abstract--The normal spectral emittance ($\lambda = 0.645 \mu\text{m}$) of yttrium, lanthanum, cerium, praseodymium and neodymium was determined at temperatures above 1000 K in an argon atmosphere at a pressure slightly above atmospheric. The measured normal spectral emittances are: yttrium, (solid), $\epsilon_{n\lambda} = 0.368 \pm 0.005$; (liquid), $\epsilon_{n\lambda} = 0.368 \pm 0.005$; lanthanum, (solid), $\epsilon_{n\lambda} = 0.409 \pm 0.049$; (liquid), $\epsilon_{n\lambda} = 0.257 \pm 0.015$; cerium, (liquid), $\epsilon_{n\lambda} = 0.309 \pm 0.020$; praseodymium, (solid), $\epsilon_{n\lambda} = 1.609 - 1.0964 \times 10^{-3} T \text{ (K)}$; (liquid), $\epsilon_{n\lambda} = 0.284 \pm 0.005$; neodymium, (solid), $\epsilon_{n\lambda} = 1.090 - 5.6 \times 10^{-4} T \text{ (K)}$; (liquid), $\epsilon_{n\lambda} = 0.394 \pm 0.007$.

THE DECOMPOSITION EQUILIBRIA OF PLATINUM DI- AND MONO- CHLORIDES BY THE SIMULTANEOUS TORQUE-KNUDSEN TECHNIQUE

WILLIAM G. O'BRIEN, HARVEY J. JENSEN, ROBERT N. BENEDICT,
and RENATO G. BAUTISTA

Met. Trans. B 7B: 671 (1976)

Abstract--The decomposition equilibria of platinum dichloride have been found to consist of two decomposition steps, with chlorine molecules being the vapor species for both steps. An intermediate metastable PtCl solid is formed in the first step in addition to platinum metal and chlorine molecules. The platinum dichloride decomposes incongruently, the step-wise decomposition being $\text{PtCl}_2 \rightarrow \text{PtCl} \rightarrow \text{Pt}$. The PtCl_2 decomposition reactions consist of $\text{PtCl}_2(\text{s}) = \text{PtCl}(\text{metastable s}) + 1/2 \text{Cl}_2(\text{g})$ and

$\text{PtCl}_2(\underline{s}) = \text{Pt}(\underline{s}) + \text{Cl}_2(\underline{g})$. The sum of the third law $\Delta H_{\underline{-D}, 298 \text{ K}}$ for the above two reactions is $214.637 \pm 1.963 \text{ kJ/mole}$, in very good agreement with the second law $\Delta H_{\underline{-D}, 298 \text{ K}} = 215.107 \pm 13.062 \text{ kJ/mole}$. The second decomposition step is given by the reaction $2\text{PtCl}(\text{metastable } \underline{s}) = 2\text{Pt}(\underline{s}) + \text{Cl}_2(\underline{g})$ with a third law $\Delta H_{\underline{-D}, 298 \text{ K}} = 127.356 \pm 0.791 \text{ kJ/mole}$, in excellent agreement with the second law $\Delta H_{\underline{-D}, 298 \text{ K}} = 127.509 \pm 6.154 \text{ kJ/mole}$. The calculated heat of formation of PtCl_2 is $-139 \pm 2 \text{ kJ/mole}$ and that of PtCl is $-63 \pm 1 \text{ kJ/mole}$.

THE NORMAL SPECTRAL EMITTANCE OF ERBIUM, DYSPROSIUM AND SAMARIUM ABOVE 1000 K

TERRY S. KING, DORAB N. BARIA, and RENATO G. BAUTISTA
Met. Trans. B 7B: 411 (1976)

Abstract--An apparatus for measuring the normal spectral emittance ($\lambda = 0.645\mu$) of metals with very high vapor pressures has been designed and used for erbium, dysprosium and samarium at temperatures above 1000 K. The samples are maintained in an argon atmosphere at a pressure slightly above atmospheric pressure. The measured normal spectral emittances are: Erbium, (solid), $\epsilon_{\underline{n\lambda}} = 0.372 \pm 0.011$; (liquid), $\epsilon_{\underline{n\lambda}} = 0.372 \pm 0.011$; Dysprosium, (solid), $\epsilon_{\underline{n\lambda}} = 0.631 - 1.889 \times 10^{-4} T \text{ (deg K)}$; (liquid), $\epsilon_{\underline{n\lambda}} = 0.297 \pm 0.088$; Samarium, (solid), $\epsilon_{\underline{n\lambda}} = 0.437 \pm 0.030$; (liquid, estimated), $\epsilon_{\underline{n\lambda}} = 0.437 \pm 0.03$.

IV. FLUID DYNAMICS

MASS TRANSFER AND INTERNAL CIRCULATION IN FORMING DROPS

LAWRENCE BURKHART, P. W. WEATHERS and P. C. SHARER
AIChE J. 22: 1090 (1976)

Abstract--The presence of internal circulation in forming liquid drops has a significant effect on mass transfer rates. For the systems

studied, no circulation was observed below a Reynolds number of 9.7. For Reynolds numbers between 9.7 and 34.4, transition from zero circulation to complete circulation during the entire drop formation period occurred. In studies on the rate of mass transfer from fixed volume drops with forced internal circulation, increases in mass transfer rates were found at Reynolds numbers which corresponded to those observed for the development of internal circulation patterns within the drop.

SCALE-UP OF A MIXED-SETTLER EXTRACTOR USING A UNIT OPERATIONS APPROACH

DAVID C. LINDHOLM and RENATO G. BAUTISTA
Trans. Soc. Mining Engr., AIME 260: 1 (1976)

Abstract--The results of scale-up studies on a continuous, multi-stage horizontal mixer-settler extractor are presented. The chemical and mechanical system involves the separation of lanthanum from a mixture of rare earth chlorides using di(2-ethylhexyl) phosphoric acid as the solvent and dilute HCl as a scrub solution in a bench scale extractor. Each stage has a hold-up of 2.6 l. A single stage unit is utilized for scale-up studies. Results are obtained on four sizes of geometrically similar units, the largest being six times the volume of the original bench size. A unit operations technique is chosen so that mixing and settling can be examined independently. Variables examined include type of continuous phase, flow rate of inlet streams, and power input to the mixer. Inlet flow-rate ratios are kept constant for all tests. Two potential methods of unbaffled pump-mixer scale-up are explored; the maintenance of constant impeller tip speed and constant power input. For the settler, the previously successful method of basing design on constant flow-rate per unit cross-sectional area is used.

SURFACE CHEMISTRY AND CATALYSIS

I. HIGH TEMPERATURE CHEMISTRY

THE HIGH TEMPERATURE VAPORIZATION OF DEFECT SCANDIUM MONOSULFIDE

R. T. TUENGE, F. LAABS, and H. F. FRANZEN

J. Chem. Phys. 65: 2400 (1976)

Abstract--A high temperature vaporization study of the scandium-sulfur system has shown that a defect scandium monosulfide phase with composition $\text{Sc/S}=0.8065$ vaporizes congruently over the temperature range 1875-2220 K. High temperature mass spectrometric results show that the congruently subliming phase has two principle vaporization reactions producing $\text{ScS(g)} + \text{S(g)}$ and $\text{Sc(g)} + \text{S(g)}$. Thermodynamic results for $\text{Sc}_{0.8065}\text{S(s)}$ were obtained from both mass spectrometric and target collection investigations. Based on Mann's cross sections for atoms, additivity for molecules, and the assumption of no fragmentation, the third-law mass-spectrometric enthalpy of vaporization at 298 K of $\text{Sc}_{0.8065}\text{S}$ to form $\text{Sc(g)} + \text{S(g)}$ is 223.4 ± 4.5 kcal and to form $\text{ScS(g)} + \text{S(g)}$ is 133.8 ± 4.5 kcal; the dissociation energy D_{298}° obtained for ScS(g) is 111.1 ± 4.5 kcal. The third-law mass-spectrometric results are in good agreement with the target collection results. Ion intensity data were collected for ScS^+ as a function of time upon vaporization of stoichiometric ScS(s) at 2035 K. The third-law value obtained for the enthalpy of atomization at 298 K of $\text{Sc}_{1.0}\text{S(s)}$ is 240.2 ± 5 kcal.

XPS SPECTRA OF SOME TRANSITION METAL AND ALKALINE EARTH MONOCHALCOGENIDES

HUGO F. FRANZEN, MIRTHA X. UMANA, J. R. McCreary and R. J. Thorn
J. Solid State Chem. 18: 363 (1976)

Abstract--The first-row transition-metal monosulfides and alkaline-earth chalcogenides were studied by means of x-ray photoelectron spectroscopy. It is shown that the bonding in the alkaline earth compounds is relatively ionic with XPS evidence for significant charge separation. On the other hand, transition metal sulfides, with the exception of MnS, appear to be principally metallic with little or no charge separation. Values for the inner orbital binding energy shifts are reported for a large number of monochalcogenides.

SYNTHESIS OF DODECACARBONYLDIVANADIUM IN LOW-TEMPERATURE MATRICES

T. C. DeVORE and H. F. FRANZEN
Inorg. Chem. 15: 1318 (1976)

Abstract--The products of the cocondensation of V atoms with CO at 10 K have been investigated using ir and uv spectroscopy. Two vanadium carbonyl complexes, $V(CO)_6$ and $V_2(CO)_{12}$, have been identified and the structure of each complex was determined from the analysis of the ir spectrum. In addition, the electronic spectrum of $V(CO)_6$ has been analyzed.

SPECTROSCOPIC IDENTIFICATION OF THE BINARY DINITROGEN COMPLEXES OF CHROMIUM IN LOW-TEMPERATURE MATRICES

T. C. DeVORE
Inorg. Chem. 15: 1315 (1976)

Abstract--The products of cocondensation of Cr atoms with N_2 at 10 K have been investigated using infrared and uv-visible spectroscopy and the products of the cocondensation of Cr atoms with N_2/Ar mixtures have been investigated using infrared spectroscopy. From the behavior of each

species upon annealing and upon changing the concentration of N_2 in the matrix, the binary dinitrogen complexes $Cr(N_2)_n$, where $n = 1-6$, have been identified. Tentative structures have been determined for each complex from the analysis of the spectrum. In addition, the electronic spectrum of $Cr(N_2)_6$, obtained in a nitrogen matrix, has been analyzed. The observed Δ value for this octahedral complex was found to be $28\,800\text{ cm}^{-1}$, which clearly establishes that N_2 is a strong-field ligand.

GROWTH OF THE TRANSITION METAL OXALATES IN GELS

A. S. KHAN, T. C. DEVORE and WILFRED F. REED

J. Crystal Growth 35: 337 (1976)

Abstract--Crystalline aggregates of zinc, copper and manganese oxalates and single crystals of cobalt oxalate were prepared in silicate gel. Sodium hydrogen oxalate crystals were also obtained by reaction of the oxalic acid with the gel. The gel grown oxalates were characterized by x-ray diffraction patterns and IR spectra. Maximum silicon contamination was found to be 0.3%.

II. SURFACE CHEMISTRY AND CATALYSIS

APPLICATION OF THE FRUMKIN EQUATION TO ELECTROCAPILLARY AND CAPACITY DATA OF SOME ALIPHATIC COMPOUNDS

D. E. BROADHEAD, K. G. BAIKERIKAR, and ROBERT S. HANSEN

J. Phys. Chem. 80: 370 (1976)

Abstract--High precision electrocapillary and capacity data for n -pentanoic acid, isopentyl alcohol, and primary butyl alcohol are tested against the Frumkin equation with parameters selected to minimize root-mean-square deviations from experimental data. For electrocapillary curves with maximum adsorbate coverages less than 0.9, excellent fits were obtained (average rms

deviation for the three solutes 0.2 dyn/cm). Capacity-polarization curves are much more highly structured and therefore more severely test adsorption theories; deviations between experiment and theory were plainly evident in all systems and the average rms deviation for the three solutes was $1.5 \mu\text{F}/\text{cm}^2$. Parameters chosen to best fit electrocapillary curves were in fair agreement with those chosen to best fit capacity curves but interchange of parameter sets led to noticeably poorer fits (average rms deviations about 0.6 dyn/cm and $2 \mu\text{F}/\text{cm}^2$, respectively). Substantially poorer fits resulted if data corresponding to maximum coverages in excess of 0.9 were included.

ETHYLENE HYDROGENATION ON EVAPORATED IRIIDIUM FILMS

PAUL MAHAFFY, PAUL B. MASTERSON and ROBERT S. HANSEN
J. Chem. Phys. 64: 3911 (1976)

Abstract--The reaction of ethylene with hydrogen to form ethane and methane is studied over evaporated iridium thin film catalysts. The rate law obtained at total pressures up to 1000 μ and temperatures between 110 and 200 K is of the form: $\underline{R} = \underline{K} \underline{P}^0_{\text{C}_2\text{H}_4} \underline{P}^{1/2}_{\text{H}_2} \exp(-3.3 \text{ kcal/mole}/\underline{RT})$, where 0 and 1/2 are the reaction orders in ethylene and hydrogen, respectively. Over a wider temperature range (up to 100°C) the reaction is characterized by the use of ^{13}C labeled ethylene or deuterium in the place of hydrogen. The kinetic results taken in conjunction with the isotope studies are consistent with a Langmuir-Hinshelwood hydrogenation mechanism involving the half-hydrogenated ethyl species C_2H_5 (a) first postulated by Polanyi. At temperatures greater than ~ 150 K the rate of a surface dehydrogenation reaction becomes significant. The extent of this surface reaction can be determined by monitoring the amount of ethane produced when only ethylene is dosed on a

clean IR film or by observing nonlinearities in the Arrhenius plots when both hydrogen and ethylene are dosed. Production of methane from ethane decomposition at 373 K is poisoned by ethylene adsorption. Film area as measured by both hydrogen adsorption and catalytic activity is proportional to film thickness for average thicknesses of 30 to 200 Å.

MAGNETIC SPECIFIC HEAT OF THE NEARLY-ONE-DIMENSIONAL SYSTEM
TETRAMETHYL AMMONIUM NICKEL TRICHLORIDE (TMNC)

K. Kopinga, T. de Neef, W. J. M. de Jonge and B. C. GERSTEIN
Phys. Rev. B 13: 3953 (1976)

Abstract--The specific heat of tetramethyl ammonium nickel trichloride (TMNC) for $3.5 < T < 20$ K has been analyzed using the scaled lattice contribution of the isomorphic cadmium and manganese compounds and a magnetic contribution represented by the Hamiltonian $\mathcal{H} = -2J \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - D \sum_i [S_{iz}^2 - S(S+1)/3]$. The resulting parameter values $J/k = +1.7 \pm 0.3$ K, and $D/k = -3.3 \pm 0.5$ K are qualitatively in agreement with the results from susceptibility measurements.

CRYSTAL STRUCTURE AND MAGNETIC SUSCEPTIBILITY OF $[(CH_3)_3NH]_3Mn_2Cl_7$

Ruth E. Caputo, Sue Roberts, Roger D. Willett and BERNARD C. GERSTEIN
Inorg. Chem. 15: 820 (1976)

Abstract--The crystal structure of $[(CH_3)_3NH]_3Mn_2Cl_7$ has been determined and the magnetic susceptibility of the compound measured. The salt belongs to the polar hexagonal space group $P6_3/mc$ with $a = 14.509(19)$ and $c = 6.415(7)$ Å, $Z = 2$. The structure consists of linear chains of face-shared $MnCl_6$ octahedra and discrete $MnCl_4^2$ tetrahedra which are separated by the trimethylammonium ions. The susceptibility data can be explained by a model consisting of the susceptibility of a system of linear chains together with the susceptibility of the discrete $MnCl_4^2$ tetrahedra.

MOLECULAR, MATHEMATICAL AND GEOSCIENCES

Fundamental Interactions

RADIATION SCIENCES

I. PHOTOCHEMISTRY AND SPECTROSCOPY

POLARITONS AND PERFECT CRYSTAL BEHAVIOR OF NAPHTHALENE

SUSAN S. ROBINETTE and GERALD J. SMALL

J. Chem. Phys. 65: 837 (1976)

Abstract--We report optical transmission data on pure and strain-free naphthalene crystals which provide strong evidence for the existence of polariton states and the correctness of the fundamental light absorption mechanism predicted by the polariton model for molecular crystals.

RESONANT ABSORPTION IN STATIONARY AND NONSTATIONARY FIELDS

V. SETHU RAMAN and G. J. SMALL

J. Chem. Phys. 64: 3359 (1976)

Abstract--Response of a two-level atom, relaxing owing to strong thermalizing collisions, in a weak near-resonant pulsed radiation field is examined using the second order perturbation solution of the optical Bloch equations. Dependence of the rate of absorption on the collisional relaxation time of the atom, the correlation time, pulse width, and the degree of detuning of the incident field are discussed.

II. RADIATION AND SOLID STATE SPECTROSCOPY

Cis-DICHLORODIAMMINEPLATINUM(II). AQUATION EQUILIBRIA AND ISOTOPIC EXCHANGE OF CHLORIDE LIGANDS WITH FREE CHLORIDE AND TETRACHLOROPLATINATE(II)

K. W. LEE and D. S. MARTIN, Jr.

Inorg. Chim. Acta 17: 105 (1976)

Abstract--The equilibrium quotients for the first and second aquation steps of $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ have been determined by a titration technique. At 25.0°C and an ionic strength of 0.318M the first and second aquation equilibrium constants are: $K_1 = 3.63 \pm .22 \times 10^{-3} \text{M}$, $\Delta H_1^\circ = 3.4 \text{ kcal}$ and $K_2 = 1.11 \pm .14 \times 10^{-4} \text{M}$, $\Delta H_2^\circ = 10 \text{ kcal}$.

The kinetics of isotopic exchange of chlorine was investigated in the ternary system: $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$, PtCl_4^{2-} , Cl^- . In addition to exchange via the route of aquation, a direct exchange of chloride between $\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2$ and PtCl_4^{2-} occurred which is described by the rate expression:

$$R = [\text{cis-Pt}(\text{NH}_3)_2\text{Cl}_2][\text{PtCl}_4^{2-}](k_{ac}' + k_{ac}''[\text{Cl}^-]^{-1}).$$

At 25°C the rate constants were $k_{ac}' = 3.0 \times 10^{-4} \text{M}^{-1} \text{sec}^{-1}$ and $k_{ac}'' = 9.0 \times 10^{-5} \text{sec}^{-1}$.

POLARIZED CRYSTAL ABSORPTION SPECTRA AND ELECTRONIC STATES OF TETRAETHYLAMMONIUM HEXABROMODIPLATINATE(II)

DON S. MARTIN, Jr., RHONDA M. RUSH, and TIMOTHY J. PETERS

Inorg. Chem. 15: 669 (1976)

Abstract--Polarized crystal electronic absorption spectra are reported at 300 and 15 K for normally cleaved crystals of $[\text{N}(\text{C}_2\text{H}_5)_4]_2\text{Pt}_2\text{Br}_6$. The spectra provide the polarization of the transitions with respect to the three molecular axes of the $\text{Pt}_2\text{Br}_6^{2-}$ ion. The excited states have been assigned under the D_{2h} point group symmetry of the ion. There is sufficient

delocalization of the d electrons that both spin-forbidden and spin-allowed $d \leftarrow d$ transitions have strongly enhanced intensities and have dipole-allowed character in contrast to the PtBr_4^{2-} ion. Although the energies of $d \leftarrow d$ transitions are similar for PtBr_4^{2-} and $\text{Pt}_2\text{Br}_6^{2-}$, $M \leftarrow L$ charge-transfer transitions occur at lower energies for the dimeric ion. The polarization of these intense transitions indicates that they correspond to electron transfers from terminal bromides.

INVESTIGATIONS OF QUADRUPLE BONDS BY POLARIZED CRYSTAL SPECTRA. 2. QUADRUPLY BONDED TETRA- μ -GLYCINE-DIMOLYB-DENUM(II) SULFATE TETRAHYDRATE

F. A. COTTON, DON S. MARTIN, THOMAS R. WEBB and TIMOTHY J. PETERS

Inorg. Chem. 15: 1199 (1976)

Abstract--Polarized single crystal spectra have been recorded for the compound $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ over the first absorption band through the region $20\,000\text{--}25\,000\text{ cm}^{-1}$. The crystal spectra at 15 K have revealed the vibrational structure for this band in each of the two polarizations with respect to the molecular axes. For $\underline{z}$ polarization (parallel to the Mo-Mo bond) a weak progression of four lines begins at $20\,570\text{ cm}^{-1}$. A more intense progression consisting of nine lines begins at $21\,510\text{ cm}^{-1}$. For $\underline{x}$, $\underline{y}$ polarization two intense progressions are seen: one beginning at $21\,790\text{ cm}^{-1}$ has seven lines, and one beginning at $21\,930\text{ cm}^{-1}$ has six lines. The average separation of lines in each progression is about 343 cm^{-1} . It is concluded that the transition is forbidden under the local symmetry of $\underline{D}_{4h}$. The weak band in $\underline{z}$ polarization is attributed to degradation of the local $\underline{D}_{4h}$ symmetry to the crystallographic site symmetry of $\underline{S}_4$. The more intense progression in $\underline{z}$ and the two progressions in $\underline{x}$, $\underline{y}$ polarization are

attributed to vibronic excitation by asymmetric vibrations under the D_{4h} symmetry. Accordingly, the absorption band cannot be assigned to the $\delta \rightarrow \delta (^1A_{1g} \rightarrow ^1A_{2u})$ transition under D_{4h} symmetry.

ELECTRONIC SPECTRA OF CRYSTALS OF DIMOLYBDENUM TETRAFORMATE AND THE TETRASULFATODIMOLYBDENUM(II) ION

F. A. COTTON, DON S. MARTIN, PHILLIP E. FANWICK, TIMOTHY J. PETERS, and THOMAS R. WEBB
J. Am. Chem. Soc. 98: 4681 (1976)

Abstract--Crystal polarization measurements have been made on dimolybdenum tetraformate at 15 K, in the same region as previously studied for $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 2H_2O$. The results are much more complex because the Mo_2 units are not all parallel, but appear to be entirely consistent with those for the glycinate. It is concluded, therefore, that the spectra of the glycinate can be regarded as representative for $Mo_2(O_2CR)_4$ species in general. For $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ it is shown that the band at $19,400\text{ cm}^{-1}$ has pronounced polarization parallel to the molecular (Mo=Mo) axis and that its intensity is essentially temperature-independent from 300 K to 15 K. These data suggest that the band may be assigned to the $\delta \rightarrow \delta$ transition.

CHEMICAL PHYSICS

I. STATISTICAL MECHANICS OF GASEOUS SYSTEMS

ON THE NONEQUILIBRIUM DISTRIBUTION OF ADATOMS RESULTING FROM DISSOCIATIVE ADSORPTION OF A DIATOMIC GAS

DAVID K. HOFFMAN
J. Chem. Phys. 65: 95 (1976)

Abstract--Kinetic equations governing the distribution of adatoms resulting from irreversible, dissociative adsorption of homonuclear diatoms onto a two-dimensional lattice are derived. Desorption and atomic skating

are ignored, which allows the problem to be conveniently formulated from a molecular viewpoint. The rate constant for adsorption is assumed to be of an Arrhenius form with an activation energy which consists of an additive contribution from the interaction of the adsorbing molecule with each adatom on the surface. Special attention is paid to the relationship between the molecular distribution resulting from irreversible adsorption and the equilibrium molecular distribution. The kinetic equations are solved as a power series in the covering fraction; the coefficients involve molecular cluster diagrams similar to those in equilibrium, virial expansions. Comparison of the non-equilibrium and equilibrium covering fraction expansions of the molecular pair distribution functions is made, and an illustrated example is considered for a case where the functions and their expansions can be evaluated exactly. Finally, the effect of the nonequilibrium distribution of adatoms on the configurational contribution to the thermodynamic properties of the adsorbate is discussed.

II. MASS SPECTROSCOPY, ION SOURCE CHEMISTRY

A MASS SPECTROMETER FOR THE CHARACTERIZATION OF NEUTRAL SPECIES PRODUCED IN THE ELECTRON BOMBARDMENT OF GASES

JOHN R. REEHER, GERALD D. FLESCH and HARRY J. SVEC

Internat. J. Mass Spectrometry Ion Phys. 19: 351 (1976)

Abstract--A mass spectrometer which permits the direct study of neutral species produced by the electron bombardment of gases is described. Functionally, it consists of an ion source with two independent electron beams, a quadrupole mass filter, and a phase-sensitive ion detector. The instrument provides for automatic scanning and recording of mass spectra and ionization

efficiency data for the neutral species produced in one electron beam (pulsed at 260 Hz) and subsequently ionized in the other electron beam.

The mass spectrum of the neutral species obtained from the electron bombardment of benzene, along with the ionization efficiency data for the neutral species, are presented to demonstrate the quality of the data obtained.

THE MASS SPECTRA AND IONIZATION POTENTIALS OF THE NEUTRAL FRAGMENTS PRODUCED DURING THE ELECTRON BOMBARDMENT OF AROMATIC COMPOUNDS

JOHN R. REEHER, GERALD D. FLESCH and HARRY J. SVEC
Organic Mass Spectrometry 11: 154 (1976)

Abstract--A mass spectrometer equipped with a dual ionization chamber ion source has been used to characterize directly the neutral species produced in the dissociative ionization of gases by electron impact. Neutral fragment mass spectra have been obtained for the electron ionization and fragmentation of benzene, toluene, o-xylene, m-xylene, p-xylene, mesitylene and isotopically labeled toluene. The neutral fragment mass spectra correlate well with the structures of the molecules. The abundant species in the neutral fragment mass spectra also correlate reasonably well with the abundant complementary positive ions of the normal mass spectra. Ionization potentials have been determined for the abundant neutral species produced. Where comparisons with values reported elsewhere are possible, the agreement is usually within ± 0.2 eV or less.

III. MOLECULAR BONDING THEORY

MCSCF STUDIES OF CHEMICAL REACTIONS: NATURAL REACTION ORBITALS AND LOCALIZED REACTION ORBITALS

KLAUS RUEDENBERG and KENNETH R. SUNDBERG

Quantum Science, eds., Jean-Louis Calais, Osvaldo Goscinski, Jan Linderberg and Yngve Ohrn (New York: Plenum Publishing Corp., 1976) pp. 505-515

Abstract--In order to gain conceptual insight into the nature of the change in bonding patterns during chemical reactions an interpretative analysis of wavefunctions in the full optimized reaction space has been developed which is based on the novel concepts of natural and localized reactions orbitals. These novel orbitals can be extracted from a completely general multiconfigurational wave-function in an unambiguous manner and their deformations and occupation number changes are illuminating interpretative tools. They yield information about those molecular orbitals which dominate the electronic structure changes during the reaction, as well as about those atomic hybrid orbitals which describe the participation of each atom in the rearrangement of bonds.

IV. CRYSTALLOGRAPHY OF ORGANIC AND BIOLOGICAL MATERIALS

AUSTIN, A NOVEL POLYISOPRENOID MYCOTOXIN FROM ASPERGILLUS USTUS

K. K. Chexal, JAMES P. SPRINGER, JON CLARDY, Richard J. Cole, Jerry W. Kirksey, Joe W. Dorner, Horace G. Cutler, and Bill J. Strawter J. Am. Chem. Soc. 98: 6748 (1976)

Abstract--The discovery of the highly toxic and carcinogenic aflatoxins has generated considerable interest in other toxins produced by fungi contaminating stored foodstuffs. Steyn has reported austamide and substances biogenetically related to it as toxic metabolites from a strain of Aspergillus

ustus. Vleggaar, Steyn, and Nagel have described austdiol as the major toxin from the same source. We now report the highly unusual structure 1 for the major toxin elaborated by a strain of A. ustus found on stored black-eyed peas (Vigna sinensis). We propose the trivial name austin for this metabolite.

MAMANINE AND POHUKULINE, TWO UNPRECEDENTED QUINOLIZIDINE ALKALOIDS FROM SOPHORA CHRYSOPHYLLA

Mavis M. Kadooka, Mildred Y. Chang, Hiroshi Fukami, P. J. Scheuer, JON CLARDY, BARBARA A. SOLHEIM, and JAMES P. SPRINGER
Tetrahedron 32: 919 (1976)

Abstract--From the bark of the endemic Hawaiian tree Sophora chrysophylla Seem. we have isolated two unprecedented quinolizidine alkaloids, mamine (4) and pohakuline (5). Both bases are 1-hydroxymethylene-quinolizidines which are linked at C-3 to α -pyridone or α -piperidone moieties. The alkaloids may be intermediates in a heretofore unknown biogenetic pathway of Sophora alkaloids.

NASUTE TERMITE SOLDIER FRONTAL GLAND SECRETIONS. I. STRUCTURE OF TRINERVI-2 β , 3 α , 9 α -TRIOL 9-O-ACETATE, A NOVEL DITERPENE FROM TRINERVITERMES SOLDIERS

Glenn D. Prestwich, Steven P. Tanis, JAMES P. SPRINGER and JON CLARDY
J. Am. Chem. Soc. 98: 6061 (1976)

Abstract—The defensive secretions ejected from the nozzle-like frontal glands of Trinervitermes and Nasutitermes soldiers (Isoptera: Termitidae: Nasutitermitinae) have been reported to contain polyisoprenoids of unknown structure dissolved in monoterpene hydrocarbons. These sticky secretions mechanically disable ant predators and also appear to possess some systemic toxicity to the ants.

We wish to report the results of x-ray crystallographic studies carried out on one of the major constituents, "TG-2", of the soldier secretions of Trinervitermes gratus Sjöstedt. It is a novel diterpene skeleton with a bridgehead double bond in an 11-membered ring.

PHOSPHORUS ESTER BASICITY DEPENDENCE ON CONSTRAINT. CRYSTAL AND MOLECULAR STRUCTURES OF P(OCH₂)₃CCH₂Br AND

D. S. Milbrath, J. P. SPRINGER, J. C. CLARDY and J. G. VERKADE
J. Am. Chem. Soc. 98: 5493 (1976)

Abstract--Structural parameters of the title compounds along with those of similar systems reported earlier can be related by means of hybridization considerations to the decrease in basicity of phosphorus realized upon constraint of the alkoxy groups. It is concluded that the :P(OCH₂)₃CR cage is essentially unstrained but that oxidation to O=P(OCH₂)₃CR induces stress primarily in the POC angles. In O = $\overline{\text{P}(\text{OCH}_2)_2\text{C}(\text{CH}_3)\text{O}}$ (2), however, compression of both the OPO and POC angles is observed. The unit cells were

found to be orthorhombic, $P_{2_1^2_1^2_1}$, $a = 5.823(1)$, $b = 7.956(1)$, and $c = 16.695(2) \text{ \AA}$, and $Pnma$, $a = 8.928(1)$, $b = 8.148(1)$, and $c = 8.410(1) \text{ \AA}$, for $P(OCH_2)_3CCH_2Br$ and 2, respectively. Final R factors using anisotropic temperature factors with inclusion of the hydrogen positions are 0.036 and 0.028 for 602 and 379 reflections, respectively, measured on a Syntex $P2_1$ diffractometer.

THE STRUCTURE OF CORYLIFURAN, A CLERODANE-TYPE DITERPENE FROM CROTON CORYLIFOLIUS LAM

B. A. Burke, W. R. Chan, E. C. Prince, P. S. Manchand, NANCY EICKMAN, and JON CLARDY
Tetrahedron 32: 1881 (1976)

Abstract--The structure and stereochemistry of corylifuran, a clerodane-type diterpene from Croton corylifolius Lam, have been determined as 2 by chemical and spectroscopic data and x-ray crystallographic analysis.

SYNTHESIS AND STRUCTURE OF DICARBONYLDI- η -CYCLOPENTADIENYL BIS (μ -THIOCARBONYL)DIIRON, A THIOCARBONYL ANALOG OF THE DICARBONYL- η -CYCLOPENTADIENYLIRON DIMER

Jan Dunker, JANET S. FINER, JON CLARDY, and ROBERT J. ANGELICI
J. Organomet. Chem. 114: C49 (1976)

Abstract--Sodium hydride reduction of $(\eta-C_5H_5)Fe(CO)_2(CS)^+$ gives cis- and trans- $[(\eta-C_5H_5)Fe(CS)(CO)]_2$. The trans isomer slowly converts to a cis-trans mixture in xylene solution. An x-ray structural study of the cis isomer shows the CS groups to be in the bridging positions, but otherwise, its structure is nearly identical to that of cis- $[\eta-C_5H_5)Fe(CO)_2]_2$. The cis isomer reacts with CH_3OSO_2F to give the compound, $(\eta-C_5H_5)_2Fe_2(CSCH_3)(CS)(CO)_2^+$, with a methylated bridging thiocarbonyl group.

2-OXO-2-(BIS- β -CHLOROETHYLAMINO)-1- β -CHLOROETHYLAMINO-1,3,2-AZA-OXAPHOSPHORINANE, C₉H₁₈O₂PN₂Cl₃

H. A. Brassfield, J. C. CLARDY and J. G. VERKADE
Cryst. Struct. Comm. 5: 417 (1976)

Abstract--The strong anti cancer action of the phosphamide series shown below has elicited keen interest in the solid state structural properties of these molecules.

ISOLATION AND STRUCTURE DETERMINATION OF THE MYCOTOXIN, CHAETOGLOBOSIN C, A NEW [13] CYTOCHALASIN

JAMES P. SPRINGER, JON CLARDY, John M. Wells, Richard J. Cole, R. D. Macfarlane and D. F. Tongeson
Tet. Lett. 17: 1355 (1976)

Abstract--As part of our continuing program on the isolation and characterization of fungal toxins we wish to report the structure of chaetoglobosin C (1), a [13]-cytochalasin. In recent years the cytochalasins have received considerable scrutiny because of their wide range of biological effects especially cytostatic activity.

A NOVEL DITERPENE FROM *DOLLABELLA CALIFORNICA*

Chris Ireland, D. J. Faulkner, JANET FINER and JON CLARDY
J. Am. Chem. Soc. 98: 4664 (1976)

Abstract--The sea hare *Dollabella californica* Sterns, a large soft-bodied opisthobranch mollusk, was collected at Isla Partida, Gulf of California. The digestive gland of *Dollabella*, like that of *Aplysia californica*, contained a number of terpenoid compounds which are probably of dietary origin. The major components of the digestive gland extracts are a series of diterpenes which appear to be closely related. We wish to report the structural determination by single-crystal x-ray diffraction analysis of a diterpene 1 having a novel 5,11-bicyclic carbon skeleton.

Figure 1. A computer generated perspective drawing of 1. Hydrogens are not shown, and no absolute stereochemistry is implied.

SPHAEROCOCCENOL A: A NEW REARRANGED BROMO-DITERPENE FROM THE RED ALGA *SPHAEROCOCCUS CORONOPHOLIUS*

William Fenical, JANET FINER and JON CLARDY
Tet. Lett. 10: 731 (1976)

Abstract--Biosynthesis involving bromination mechanisms is now recognized as a characteristic of at least nine families of the red seaweeds (Rhodophyta). While bromine-containing diterpenes are not common among these algae, examples of two ring systems, concinndiol and iniediol, are

elaborated only by Laurencia species. We wish to report herein the structure of a new bromo-diterpene obtained from extracts of the red seaweed Sphaerococcus coronopifolius (Good. and Woodw.) Ag. (Sphaerococcaceae).

This metabolite appears to result from a methyl migration of a tail to tail diterpene precursor or from more substantial molecular rearrangements.

STRUCTURE AND SYNTHESIS OF VERRUCULOTOXIN, A NEW MYCOTOXIN FROM PENICILLIUM VERRUCULOSUM PEYRONEL

JAMES G. MACMILLAN, JAMES P. SPRINGER, JON CLARDY, Richard J. Cole and Jerry W. Kirksey
J. Am. Chem. Soc. 98: 246 (1976)

Abstract--The fungus Penicillium verruculosum, peyronel, isolated from green peanuts, produces a toxic metabolite with an LD₅₀ of 20 mg/kg (oral, 1-day-old cockerel). Acute toxicity was characterized by ataxia, prostration, and complete lack of muscular coordination. In spite of these severe signs, the animals' eyes were open, and they appeared to be otherwise alert for the next hour. Isolation procedures, ir, NMR, MS and uv data for this metabolite have been reported in a preliminary paper, and the trivial name verruculotoxin was proposed. We wish now to report the absolute stereostructure of verruculotoxin (1) from a combination of x-ray diffraction analysis and synthesis.

V. ATOM, MOLECULAR AND FREE RADICAL CROSSED BEAM KINETICS

ALKALI ATOM CHEMILUMINESCENCE FROM CROSSED BEAMS

REACTIONS OF $\text{Hg}(^3\text{P}_{0,2})$ + ALKALI HALIDES

Lambert C.-H. Loh and RONALD R. HERM
Chem. Phys. Lett. 38: 263 (1976)

Abstract--A beam of $6\ ^3\text{P}_{0,2}$ metastable mercury atoms has been crossed by a velocity-selected beam of LiI, NaI, or NaBr and the resulting fluorescence from the $\text{Li}(2^2\text{P})$ or $\text{Na}(3^2\text{P})$ levels has been measured. In this manner, the cross section for reactive production of these excited alkali atoms has been found to decrease rapidly with increasing collision speed, g , ($g = 0 - 1\text{ km/s}$) although a secondary rise at high g is also observed for LiI.

CROSSED BEAMS CHEMISTRY: $\text{Ba}(^1\text{S}) + \text{SO}_2(^1\text{A}) \rightarrow \text{BaO}(^1\Sigma^+) + \text{SO}(^3\Sigma^-)$

R. BEHRENS, Jr., A. FREEDMAN, R. R. HERM and T. P. PARR
J. Am. Chem. Soc. 98: 294 (1976)

Abstract--The laboratory (LAB) angular distribution of BaO product produced by crossing a thermal Ba beam with an SO_2 nozzle beam has been measured in a molecular beam apparatus equipped with an electron bombardment ionizer-quadrupole mass filter "universal" detector. The center-of-mass (CM) product angular distribution must possess approximate symmetry with respect to forward versus backward scattering in order to account for the bimodal LAB angular distribution which is observed. This symmetric CM distribution indicates that the reaction proceeds (under single collision conditions) via formation of a BaSO_2 complex which persists for at least several rotational periods. The mechanism of this fast, spin-forbidden bi-

molecular reaction is briefly discussed in terms of the occurrence of this long-lived reaction intermediate.

CROSSED MOLECULAR BEAM METATHESIS: ALKALINE EARTH DIHALIDES + Cl_2 AND HCl

ANDREW FREEDMAN, RICHARD BEHRENS, Jr., TIMOTHY P. PARR and RONALD R. HERM
J. Chem. Phys. 65: 4739 (1976)

Abstract—Exploratory crossed molecular beam studies of bimolecular reactions of alkaline earth dihalides with halogen containing compounds are reported. The c.m. product distribution is symmetric about $\theta = 90^\circ$ for the $\text{BaI}_2 + \text{Cl}_2$ halogen-exchange reaction indicating formation of a collision complex which persists for at least a few rotational periods. The data are consistent with, but do not establish, formation of a similar complex in the $\text{SrI}_2 + \text{Cl}_2$ reaction and with a statistical loose transition state energy partitioning in both reactions. The $\text{BaI}_2 + \text{HCl} \rightarrow \text{BaICl} + \text{HI}$ reaction is direct, favoring backscattering of the metal atom. Relative total reaction cross sections for the $\text{MX}_2 + \text{Cl}_2$ halogen-exchange reactions decrease as 1.0:0.45: < 0.007 when M is varied from Ba to Sr to Mg. All of these observations support an ion-pair adduct model which was previously advanced to interpret facile four-center exchange reactions of cesium halides with diatomic halogens. This model, which qualitatively correlated observed trends with reactant electronic structure, pictures these present reactions as $(\text{MI})^+ \text{I}^- + \text{Cl}_2 \rightarrow (\text{MI})^+ - (\text{Cl}-\text{I}-\text{Cl})^- \rightarrow \text{products}$ and $(\text{MI})^+ \text{I}^- + \text{HCl} \rightarrow (\text{MI})^+ (\text{I}-\text{H}-\text{Cl})^- \rightarrow \text{MICl} + \text{HI}$.

PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS
MOLECULAR BEAM KINETICS: $\text{Li} + \text{CH}_3\text{NO}_2$, CCl_4 , AND CH_3I

Charlotte M. Sholeen and RONALD R. HERM

J. Chem. Phys. 65: 5398 (1976)

Abstract--Recoil velocity spectra of LiNO_2 , LiCl , and LiI reactively scattered from crossed thermal beams of Li and CH_3NO_2 , CCl_4 , or CH_3I have been measured by positioning a combination of an inhomogeneous electromagnet (to deflect aside nonreactively scattered Li atoms) and a slotted disk velocity analyzer between the beam collision zone and surface ionization detector. Transformation of these data into the center-of-mass (CM) coordinate system provides contour maps of the differential reaction cross sections. The CM product angular distributions from the three reactions are quite different: $\text{Li} + \text{CH}_3\text{I}$ favors backward scattering (i.e., a reversal in Li atom direction during the reaction) although the CM distribution is poorly resolved due to unfavorable kinematics; $\text{Li} + \text{CCl}_4$ favors sideways scattering; and $\text{Li} + \text{CH}_3\text{NO}_2$ favors forward scattering. The product recoil energy distributions are quite similar for all three reactions and indicate potential energy surfaces with substantial repulsion between the products. These results are discussed in relation to previous work on related reactions and interpreted in terms of the electronic structure of ion-pair intermediates.

PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS
MOLECULAR BEAMS KINETICS: $\text{Li} + \text{Cl}_2$, Br_2 AND ICl

Charlotte M. Sholeen, Lara A. Gunde and RONALD R. HERM
 J. Chem. Phys. 65: 3223 (1976)

Abstract--An inhomogeneous deflecting magnet and slotted disk velocity analyzer combination has been used to deflect aside nonreactively scattered Li atoms and thereby measure velocity distributions of LiBr and LiCl reactively scattered from crossed thermal beams of Li and Br_2 or Cl_2 . Transformation of these data into the center-of-mass coordinate system provides contour maps of the differential reactive cross sections which indicate that the $\text{Li} + \text{Br}_2$ and the $\text{Li} + \text{Cl}_2$ reactions have the following features in common: (a) The reaction mechanisms are direct; (b) The product angular distributions are broad although forward scattering is preferred (i.e. LiX scattered in the direction of the Li velocity); (c) Small product recoil energies are most probable but the product recoil energy distributions have a long tail. There is a strong coupling of the product recoil angle and energy distributions for $\text{Li} + \text{Cl}_2 \rightarrow \text{LiCl} + \text{Cl}$ with forward scattering favoring higher product recoil energy; however, this coupling phenomenon is weak or nonexistent for the $\text{Li} + \text{Br}_2 \rightarrow \text{LiBr} + \text{Br}$ reaction. Semiquantitative observations are also presented for the $\text{Li} + \text{ICl}$ reaction. These results are discussed in relation to previous experimental and theoretical work on the reactions of alkali atoms with halogen molecules.

PRODUCT MAGNETIC DEFLECTION SLOTTED DISK VELOCITY ANALYSIS
MOLECULAR BEAMS KINETICS: $\text{Li} + \text{SnCl}_4$, PCl_3 , AND SF_6

RICHARD BEHRENS, Jr., RONALD R. HERM and Charlotte M. Sholeen
 J. Chem. Phys. 65: 4791 (1976)

Abstract--Recoil velocity spectra of the diamagnetic Li-containing products reactively scattered from crossed thermal beams of Li and SnCl_4 , PCl_3 , or SF_6 have been measured by positioning a combination of an inhomogeneous deflecting electromagnet and slotted disk velocity analyzer between the collision zone and detector. Transformation of these data into the center-of-mass coordinate system provides contour maps of the differential reaction cross sections. Although data on $\text{Li} + \text{SF}_6$ are very noisy, they are consistent with a long-lived collision complex and energy equipartitioning in a loose transition state (LTS) mechanism. At some scattering angles, two peaks are observed in the measured product recoil spectra for both $\text{Li} + \text{SnCl}_4$ and $\text{Li} + \text{PCl}_3$. For $\text{Li} + \text{SnCl}_4$, indirect kinematic arguments suggest that this bimodal structure is due to $\text{LiSnCl}_3 + \text{Cl}$ and $\text{LiCl} + \text{SnCl}_3$ product channels proceeding via an LTS mechanism. For $\text{Li} + \text{PCl}_3$, this bimodal structure is attributed to production of $\text{LiCl} + \text{PCl}_2$ products via an LTS and a direct mechanism. These results are discussed in relation to previous work on these systems and interpreted in terms of the electronic structure of the ion-pair intermediates.

PRODUCT MAGNETIC DEFLECTION-SLOTTED DISK VELOCITY ANALYSIS
MOLECULAR BEAMS KINETICS: $\text{LiO}(\underline{\text{X}}^2\text{II})$ AND $\text{LiO}(\underline{\text{A}}^2\Sigma)$ FROM $\text{Li} + \text{NO}_2$

Charlotte M. Sholeen and RONALD R. HERM

J. Chem. Phys. 64: 5261 (1976)

Abstract--Product magnetic deflection-slotted disk velocity analysis establishes both $\text{LiO}(\underline{\text{X}}^2\text{II})$ and $\text{LiO}(\underline{\text{A}}^2\Sigma)$ as products of the $\text{Li} + \text{NO}_2$ bimolecular reaction. Velocity distributions of $\text{LiO}(\underline{\text{X}}^2\text{II})$ reactively scattered from crossed thermal beams of Li and NO_2 are reported. Transformation of these data into the center-of-mass coordinate system provides a contour map of the differential reactive cross section which indicates that (a) the reaction mechanism is direct, i.e., the lifetime of the LiNO_2 intermediate is less than its rotational period; (b) the $\text{LiO}(\underline{\text{X}}^2\text{II})$ product is preferentially scattered forward, i.e., in the direction defined by the Li velocity; (c) an appreciable fraction of the reaction exothermicity ($\sim 45\%$) appears as product recoil energy; and (d) distributions in product recoil angle and energy are weakly coupled with forward scattering favoring higher recoil energy.

Processes and Techniques

CHEMICAL ENERGY

I. CHEMICAL KINETICS AND REACTIVITY OF TRANSITION METAL COMPLEXES

REACTIONS OF BIS(ORGANO)(CHELATE)COBALT COMPLEXES WITH
ELECTROPHILES

JAMES H. ESPENSON, HERBERT L. FRITZ, ROGER A. HECKMAN and
 CLAUDIO NICOLINI

Inorg. Chem. 15: 906 (1976)

Abstract--Kinetics studies were conducted on the electrophilic methyl-transfer reaction of $(\text{CH}_3)_2\text{Co}(\text{chelate})$ with three electrophilic reagents, $(\text{H}_2\text{O})_2\text{Co}(\text{chelate})^+$, H_3O^+ , and $\text{C}_6\text{H}_5\text{Hg}^+$. The mechanisms of

these reactions are discussed in terms of the factors which influence the reactivity.

REACTION OF ORGANOCHROMIUM CATIONS WITH IODINE MONOBROMIDE

JAMES H. ESPENSON and GEORGE J. SAMUELS

J. Organomet. Chem. 113: 143 (1976)

Abstract--Several members of the family of $(\text{H}_2\text{O})_5\text{Cr-R}^{2+}$ complexes have been shown to react cleanly with the interhalogen molecule IBr. Products of reaction are exclusively the organic iodide RI, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$, and Br^- ; RBr and $(\text{H}_2\text{O})_5\text{Cr-Br}^{2+}$ are not formed. Rates of the IBr reactions are comparable to those of bromine and much higher than those of iodine. These results are consistent with electrophilic reactions and suggest an $\text{S}_{\text{E}}2$ mechanism.

KINETICS AND MECHANISM OF THE REACTIONS OF ORGANOCHROMIUM COMPLEXES WITH MERCURY(II) AND METHYLMERCURY(II) IONS

JOHN P. LESLIE, II and JAMES H. ESPENSON

J. Am. Chem. Soc. 98: 4839 (1976)

Abstract--Kinetics studies have been carried out on a family of organochromium complexes of the general formula $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ for the groups $\text{R} = \text{CH}_3$, C_2H_5 , $n\text{-C}_3\text{H}_7$, $\text{CH}_2\text{C}(\text{CH}_3)_3$, $i\text{-C}_3\text{H}_7$, CH_2Cl , CH_2Br , CF_3 , and $p\text{-CH}_2\text{C}_6\text{H}_4\text{Z}$ ($\text{Z} = \text{H}$, CH_3 , CN , CF_3 , and Br). These cations react with Hg^{2+} forming RHg^+ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and with CH_3Hg^+ forming CH_3HgR and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$. Reaction rates were evaluated as a function of concentration in water at 25.0° , and in a few instances in other solvents and at other temperatures. These reactions are believed to follow a bimolecular, electrophilic substitution mechanism.

KINETICS AND MECHANISM OF THE FORMATION OF ORGANOCHROMIUM(III) COMPLEXES IN THE REACTIONS OF ORGANIC PEROXIDES WITH CHROMIUM(II)

MICHAEL R. HYDE and JAMES H. ESPENSON
J. Am. Chem. Soc. 98: 4463 (1976)

Abstract--Bimolecular rate constants for reduction of a series of 17 organic peroxides, hydroperoxides, peresters, and peroxy-acids by Cr^{2+} vary within the range 7.7×10^{-6} to $3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ (25° in 1:1 v/v $\text{CH}_3\text{OH}/\text{H}_2\text{O}$). Steric factors provide the dominant influence upon reactivity, whereas electronic effects are relatively unimportant. Reaction products in both $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ and in aqueous solution are consistent with the formation of alkoxy-radical intermediates. Organochromium(III) species, $(\text{H}_2\text{O})_5\text{CrR}^{2+}$, are detected in all but the slowest reactions. The observation of a transient intermediate in reaction of perbenzoic acid with Cr(II) is attributed to formation and decomposition of phenylchromium(III) ion.

CHLORINE ATOM ABSTRACTION REACTION OF DICHLOROMETHYL-CHROMIUM(III) IONS WITH CHROMIUM(II). KINETICS AND RADIOTRACER DETERMINATIONS

JAMES H. ESPENSON and JOHN P. LESLIE, II
Inorg. Chem. 15: 1886 (1976)

Abstract--Reaction with Cr^{2+} in aqueous HClO_4 converts the complex CrCHCl_2^{2+} to $\text{CrCH}_2\text{Cl}^{2+}$, with accompanying formation of Cr^{3+} and CrCl^{2+} in equivalent amounts. Kinetic data indicate that the first and rate-limiting step ($k = 0.016 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 25.1°C) is a bimolecular halogen atom abstraction reaction of CrCHCl_2^{2+} and Cr^{2+} , forming CrCl^{2+} and CrCHCl^{2+} . The latter intermediate, according to chromium-51 tracer results, rapidly exchanges with Cr^{2+} via an intermediate $\text{Cr}_2\text{CHCl}^{4+}$, the latter subsequently being converted to Cr^{3+} and $\text{CrCH}_2\text{Cl}^{2+}$ in a protonolysis step. The chemistry

of these reactions is discussed, and reference is made to the observation of an intensely absorbing transient formed at lower $[H^+]$ (0.01–0.05 M), which is believed to be a nonproductive intermediate lying off the main reaction pathway. A mechanism to account for these observations is proposed.

II. PROPERTIES OF RARE EARTH ELECTROLYTES

DENSITIES AND THERMAL EXPANSION OF SOME AQUEOUS RARE EARTH CHLORIDE SOLUTIONS BETWEEN 5° AND 80° C. II. $SmCl_3$, $GdCl_3$, $DyCl_3$, $ErCl_3$, AND $YbCl_3$

ANTON HABENSCHUSS and FRANK H. SPEDDING
J. Chem. Eng. Data 21: 95 (1976)

Abstract—A dilatometric method is used to determine the densities of aqueous solutions of $SmCl_3$, $GdCl_3$, $DyCl_3$, $ErCl_3$, and $YbCl_3$ from approximately 0.1 to 3.5 molal, and from 5° to 80°C at 5° intervals. Temperature and concentration dependent empirical equations representing the apparent molal volumes are given. The partial molal volumes, coefficients of thermal expansion, and apparent and partial molal expansibilities derived from these fits are discussed in terms of the ion-ion and ion-solvent interactions in these solutions and their dependence on ion size. The previously reported two-series effect in the apparent and partial molal volume properties at 25°C across the rare earth series, although modified, persists from 5° to 80°C at all concentrations. The coefficients of thermal expansion and apparent and partial molal expansibilities increase with decreasing ionic radius of the rare earth cation, with a reversal in this trend in the middle of the rare earth series.

HEATS OF DILUTION OF SOME AQUEOUS RARE EARTH ELECTROLYTE SOLUTIONS AT 25°C. 2. RARE EARTH NITRATES

FRANK H. SPEDDING, JOHN L. DERER, MICHAEL A. MOHS, and JOSEPH A. RARD

J. Chem. Eng. Data 21: 474 (1976)

Abstract--The heats of dilution of the aqueous trinitrates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu have been measured from dilute solution to saturation at 25°C. The integral heats of solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Er}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Lu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in water have also been determined. The heat of dilution data were fitted directly to semiempirical polynomials and these polynomials were used to calculate apparent and partial molal heat quantities. The results are compared to available thermodynamic and transport data for the rare earth nitrates.

ISOPIESTIC DETERMINATION OF THE ACTIVITY COEFFICIENTS OF SOME AQUEOUS RARE EARTH ELECTROLYTE SOLUTIONS AT 25°C. 1. THE RARE EARTH CHLORIDES

FRANK H. SPEDDING, HERMAN O. WEBER, VICTOR W. SAEGER, HARRY H. PETHERAM, JOSEPH A. RARD, and ANTON HABENSCHUSS
J. Chem. Eng. Data 21: 341 (1976)

Abstract--The osmotic coefficients of the aqueous trichlorides of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y have been determined from 0.1 m to saturation at 25°C. Semiempirical least-squares equations were obtained for the osmotic coefficients as a function of molality and these equations were used to calculate water activities and mean molal activity coefficients. The water activities of the light rare earth chlorides at constant molalities are higher than for the heavy rare earths, while the mean molal activity coefficients are larger for the heavy rare earths than for

the light ones. The above effects are discussed in terms of changes in the cationic radii and hydration of the rare earth ions.

A REVIEW OF THE OSMOTIC COEFFICIENTS OF AQUEOUS H_2SO_4 AT 25°C

JOSEPH A. RARD, ANTON HABENSCHUSS, and FRANK H. SPEDDING
J. Chem. Eng. Data 21: 374 (1976)

Abstract—Among the most widely used isopiestic standards for aqueous solutions are NaCl, KCl, $CaCl_2$, and H_2SO_4 . The osmotic coefficient data for NaCl and KCl have recently been reviewed and appear to be known with a high degree of accuracy. The purpose of this paper is to reexamine and update the osmotic coefficient data for H_2SO_4 at 25°C. A semiempirical equation is given which represents the osmotic coefficients of this electrolyte to within the experimental error of the data from 0.1 to 27.7 m.

III. METALLIC AND INORGANIC HYDRIDES WITH
POTENTIAL APPLICATION IN HYDROGEN STORAGE

INVESTIGATION OF THE SYSTEMS $LaNi_5H_x$ and $LaNi_5D_x$ BY PROTON AND DEUTERON NUCLEAR MAGNETIC RESONANCE

R. G. BARNES, W. C. HARPER, S. O. NELSON, D. K. THOME and
D. R. TORGESON
J. Less-Common Metals 49: 483 (1976)

Abstract—We report on the results of a study of the $LaNi_5$ hydride and deuteride systems by means of c.w. (wide-line) nuclear magnetic resonance (NMR). The NMR spectra of samples of $LaNi_5H_x$ ($2.1 \leq x \leq 6.8$) and of $LaNi_5D_x$ ($0.4 \leq x \leq 0.7$) were obtained at resonance frequencies in the range 3–100 MHz for protons and at 16 MHz for deuterons, at temperatures in the range 4.2 – 380 K. The temperature dependence of the shape, line-width, and second moment of the proton resonance and of the nuclear quadrupole interaction parameters characterising the deuteron resonance spectrum

reflects the effects of the rapid diffusive motion of the hydrogen species at temperatures above approximately 140 K. At low temperatures (4.2 – 140 K) the proton resonance shape is distinctly non-Gaussian, with a second moment at $12.78 \pm 0.26 \text{ Oe}^2$, independent of composition, and the deuteron spectrum may be characterised by two or three quadrupole interactions, also independent of composition. Both observations indicate the existence of a single hydride phase possessing a narrow range of stoichiometry. At temperatures above approximately 270 K, the deuteron spectrum reflects only a single, weak, though well-resolved, quadrupole interaction. These results are discussed in terms of several models for hydrogen (deuterium) interstitial site occupation. Measurements are also reported bearing on the existence of an adsorbed hydrogen surface layer at temperatures in the range 4.2 – 100 K.

THERMODYNAMICS OF SOLID SOLUTION OF HYDROGEN IN Ta_6S AND Nb_{21}S_8

H. F. FRANZEN, A. S. KHAN, and D. T. PETERSON
J. Solid State Chem. 17: 283 (1976)

Abstract--Equilibrium hydrogen pressures in the system $\text{Ta}_6\text{S}-\text{H}_2$ and $\text{Nb}_{21}\text{S}_8-\text{H}_2$ have been measured for temperatures in the range 300–550°C. Data for five different temperatures were treated to obtain various thermodynamic quantities. The reactions $\text{H}(\text{S.S.}) = 1/2\text{H}_2(\text{g})$ for the systems $\text{Ta}_6\text{S}-\text{H}_2$ and $\text{Nb}_{21}\text{S}_8-\text{H}_2$ are found to be less endothermic than the respective metal-hydrogen reactions. Standard entropies of dissolved hydrogen in the sulfides are similar to those of hydrogen in the metals.

THERMODYNAMICS OF SOLID SOLUTION OF HYDROGEN IN M_2C TYPE CARBIDES OF VANADIUM AND NIOBIUM

H. F. FRANZEN, A. S. KHAN, and D. T. PETERSON
J. Solid State Chem. 19: 81 (1976)

Abstract--Equilibrium hydrogen pressures in the systems V_2C-H_2 and Nb_2C-H_2 have been determined at several temperatures in the range 400–650°C. Hydrogen pressure data were treated to obtain various thermodynamic quantities for the solutions of hydrogen in V_2C and Nb_2C . It has been found that the enthalpies of the reaction $H(S.S.) = 1/2H_2(g)$ are similar but slightly less endothermic compared to the respective metal hydrogen solid solutions. Entropies of dissolved hydrogen in V_2C and Nb_2C are also found to be similar to those of hydrogen in the respective metals.

INVESTIGATION OF THE THORIUM-ThS PHASE SYSTEM

A. S. KHAN and D. T. PETERSON
J. Less-Common Metals 50: 103 (1976)

Abstract--The phase relationships between Th and ThS have been investigated. A eutectic was found at 1630°C and 9.5 at.% sulfur. The solubility of sulfur in thorium was found to be less than 1 at.% at 1050°C. No intermediate phases between Th and ThS were found. ThS appears to become somewhat more metal-rich at higher temperatures.

IV. THERMOCHEMICAL CYCLES FOR THE PRODUCTION
OF HYDROGEN FROM WATER

THERMOCHEMICAL WATER SPLITTING: THE REVERSE DEACON REACTION AND ALTERNATIVES

DEAN L. ULRICHSON and YU-SUNG YEH
ACS Fuel Division Preprints (April, 1976)

Abstract--A number of thermochemical water splitting processes have been proposed which utilize the reverse Deacon Reaction to liberate

oxygen from water. The balance of the process is devoted to liberating the hydrogen and regenerating chlorine and other reagents. The reverse Deacon reaction is a high temperature gas phase reaction.

The thermochemical data for this reaction are quite well documented and the free energy change is zero at about 860 K. Proposals generally suggest running the reaction at 900 to 1200 K with an excess of water to minimize the recycle of chlorine.

SEPARATIONS

SEPARATIONS RESEARCH

THE CRYSTAL AND MOLECULAR STRUCTURE OF DIAQUOBIS (2,3-DI-HYDROXY-2-METHYLPROPANOATO) COPPER(II)

J. H. MILLER, J. E. POWELL, R. A. JACOBSON and S. KULPRATHIPANJA
Inorg. Chim. Acta 18: 25 (1976)

Abstract--The crystal and molecular structure of diaquobis(2,3-dihydroxy-2-methylpropanoato)copper(II) has been determined by three-dimensional x-ray analysis. The compound crystallizes in the monoclinic space group C2/c, with $\underline{a} = 5.688 \pm 0.006 \text{ \AA}$, $\underline{b} = 20.79 \pm 0.03 \text{ \AA}$, $\underline{c} = 10.569 \pm 0.016 \text{ \AA}$, $\beta = 94.55 \pm 0.06^\circ$, and $\underline{Z} = 4$. The structure was solved by direct methods and refined by full-matrix least-squares procedures to a final discrepancy factor $R = 0.090$ for 860 observed reflections ($I_o > 2\sigma(I_o)$). The geometry around the copper is distorted octahedral, with the two waters occupying the axial positions. Both ligands coordinate bidently, forming chelate rings incorporating the 2-hydroxy oxygen. The other hydroxy oxygens are not

bound to the copper. There appears to be extensive hydrogen bonding in both the a and c directions with long contacts in the b direction.

FORMATION CONSTANTS OF 2,3-DIHYDROXY-2-HYDROXYMETHYL-PROPANOATE (α, β, β' -TRIHYDROXYISOBUTYRATE) RARE EARTH CHELATE SPECIES

J. E. POWELL and S. KULPRATHIPANJA

Inorg. Chem. 15: 493 (1976)

Abstract--Our interest in determining formation constants of chelate species formed between 2,3-dihydroxy-2-hydroxymethyl-propanoate (α, β, β' -trihydroxyisobutyrate) anion (hereafter abbreviated THIB) at 0.10 ionic strength and 25°C was aroused by disparate behaviors of 2,3-dihydroxy-2-methyl-propanoate (DHIB) and 2-hydroxy-2-methylpropanoate (HIB) under these conditions. Comparing data for DHIB reported by Powell et al. and those for HIB reported by Devine indicates that the dihydroxycarboxylate ligand (DHIB) forms considerably stronger complexes with larger lanthanons (La-Eu) but appreciably weaker complexes with the smaller lanthanons (Tb-Lu) and yttrium than does the monohydroxycarboxylate anion (HIB). A similar effect was reported earlier by Stagg and Powell in the case of HIB and THIB data obtained at a fivefold higher ionic strength, but no direct comparison of results for all three ligands under comparable conditions could be made.

ANALYSIS

I. ANALYTICAL SPECTROSCOPY

INDUCTIVELY COUPLED PLASMAS AS ATOMIZATION CELLS FOR ATOMIC FLUORESCENCE SPECTROMETRY

AKBAR MONTASER and VELMER A. FASSEL

Anal. Chem. 48: 1490 (1976)

Abstract--Inductively coupled plasmas (ICP) offer promise as atomization cells for atomic fluorescence spectrometry (AFS). In this study, an ICP formed part of a modular spectroscopic system for atomic fluorescence, emission, and absorption measurements. Details on the assembly of the complete system are provided. Microwave-excited, thermostated, electrodeless discharge lamps were used as primary sources for exciting the atomic fluorescence. A minicomputer provided control of radiofrequency (RF) forward power and site of observation in the plasma, as well as data acquisition and processing. The effects of important variables on the plasma background, the atomic fluorescence signal, and signal-to noise ratio were examined. Scattering and matrix effects were also evaluated. The atomic fluorescence powers of detection for Cd, Zn, and Hg were found to be superior to those observed in emission when the same experimental facilities were used for the measurements.

SPECTROSCOPIC FLAME TEMPERATURE MEASUREMENTS AND THEIR PHYSICAL SIGNIFICANCE-IV. IMPORTANCE OF THE TRANSITION PROBABILITY FACTOR

ISAAC REIF, VELMER A. FASSEL and RICHARD N. KNISELEY

Spectrochim. Acta 31B: 377 (1976)

Abstract--A comparison of flame temperatures measured by the well-known spectroscopic "slope" method for Fe thermometric species

residing in an isothermal, optically-thin environment shows that a range of 150 K is obtained when several different sets of recommended transition probabilities are used for the determinations. A similar lack of self-consistency is also shown by the temperatures obtained from two groups of Fe lines when the same set of transition probabilities is employed. These uncertainties have not been generally recognized.

ULTRATRACE ANALYSES BY OPTICAL EMISSION SPECTROSCOPY:
THE STRAY LIGHT PROBLEM

G. F. LARSON, V. A. FASSEL, R. K. WINGE, and R. N. KNISELEY
Appl. Spectroscopy 30: 384 (1976)

Abstract--When atomic emission spectroscopy is employed for the determination of trace elements at concentrations near the detection limit, the spectral background will normally be a large fraction of the total measured signal. Precise background corrections are therefore required if accurate analyses are to be achieved. Experimental evidence is presented to document the fact that stray light may produce substantial shifts in the background signal measured with some spectrometers when the total composition of the sample changes. The data presented have been obtained with the inductively coupled plasma as an excitation source: similar effects can be expected with other excitation sources as well. Examples of various forms of stray light originating from grating defects (ghosts, near and far scatter) and defects in the design of spectrometers are presented. Various methods for the reduction, elimination or correction of stray light effects are also discussed.

PHOTOACOUSTIC SPECTROSCOPY WITH CONDENSED SAMPLES

JOHN F. McCLELLAND and RICHARD N. KNISELEY

Appl. Optics 15: 2658 (1976)

Abstract--A discussion of the photoacoustic spectroscopy of condensed matter is presented with emphasis on the role of the sample and the sample cell in the photoacoustic signal waveform. The spectrometer and sample cell are described, and an experimental evaluation of the system performance is given. Data on various samples are reported, and sample geometry, signal saturation, and scattered light effects are analyzed. The relationship between photoacoustic spectra and absorption and reflection spectra is developed.

SPECTROSCOPIC SLOPE TEMPERATURE MEASUREMENTS USING A NONCALIBRATED TUNGSTEN LAMP AS A REFERENCE LIGHT SOURCE

ISAAC REIF, VELMER A. FASSEL and RICHARD N. KNISELEY

J. Quant. Spectrosc. Radiat. Transfer 16: 471 (1976)

Abstract--The spectroscopic slope method for temperature measurements requires the calibration of the spectrometer spectral response, unless the spectral lines or band components all occur in such a small wavelength interval that the response is constant. A calibrated tungsten lamp is generally used when a spectral response calibration is required. Accurately calibrated tungsten lamps are relatively expensive and generally do not have long term stability. To circumvent this problem, a method has been developed for which noncalibrated tungsten lamps may be used as reference light sources for calibrating the spectrometer wavelength response when the true tungsten filament temperature of the reference source is equal to the unknown source temperature. Then, a plot of the proper quantities vs the lower energy

level of the spectral lines provides the source temperature. The absolute calibration of the tungsten lamp is not required.

SIMULTANEOUS DETERMINATION OF WEAR METALS IN LUBRICATING OILS BY INDUCTIVELY-COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

VELMER A. FASSEL, CHARLIE A. PETERSON, FRANK N. ABERCROMBIE, and RICHARD N. KNISELEY
Anal. Chem. 48: 516 (1976)

Abstract--The simultaneous determination of 15 different wear metals in lubricating oil by inductively-coupled plasma-atomic emission spectrometry is described. An aerosol formed from a solution of the lubricating oil in 4-methyl-2-pentanone is injected into the axial channel of an inductively-coupled plasma where the atomic spectra are excited. Detection limits range 0.0004 to 0.3 ppm for the elements studied. Low and high viscosity oils (nominally 1.9×10^{-5} to $2.45 \times 10^{-4} \text{ m}^2/\text{s}$, respectively) can be accommodated without biasing the analytical results. Approximately 1.5 min are required for completing the analytical cycle for one sample. Relevant data on precision and accuracy are included.

SIGNAL SATURATION EFFECTS IN PHOTOACOUSTIC SPECTROSCOPY WITH APPLICABILITY TO SOLID AND LIQUID SAMPLES

JOHN F. McCLELLAND and RICHARD N. KNISELEY
Appl. Phys. Lett. 28: 467 (1976)

Abstract--A simple model of the interaction between the optical and thermal properties of the sample is shown to predict signal saturation in photoacoustic spectroscopy in excellent agreement with measurements on a methylene blue dye solution. The measured onset of signal saturation as a function of the absorption is accurately predicted by the model from the sample's thermal properties. The effect of light reflection by the sample on the photoacoustic signal is discussed.

SCATTERED LIGHT EFFECTS IN PHOTOACOUSTIC SPECTROSCOPY

JOHN F. McCLELLAND and RICHARD N. KNISELEY

Appl. Optics 15: 2967 (1976)

Abstract--Photoacoustic spectroscopy has experienced considerable interest recently because it allows spectra to be measured for samples with properties not compatible with conventional transmission and reflection techniques. Many of these samples are in the form of powders, filaments, or semisolids and are associated with studies where samples must be measured in an undisturbed state. The photoacoustic spectrum measured for a sample is due to thermal deexcitation of energy states excited by light absorption from an incident monochromatic beam of variable wavelength. Since the light beam is chopped, the sample and adjacent gas are intermittently heated, causing pressure oscillations proportional to the absorption in the sample cell. These oscillations are sensed by a transducer, and the resulting signal is amplified and measured by a lock-in amplifier.

The applicability of the photoacoustic technique to a wide variety of previously difficult sample configurations has attracted the interest of workers in many fields. For this reason it is important to investigate the dependence of the photoacoustic signal on properties of both the sample and the cell. The signal dependences on sample reflectivity and the absorption coefficient have recently been discussed, and signal saturation has been predicted and observed at large values of the absorption coefficient. In this Letter observation of a scattered light contribution to the signal is reported, and a method for reducing this spurious effect is demonstrated.

COMPARISON OF INTERELEMENT EFFECTS IN A MICROWAVE SINGLE ELECTRODE PLASMA AND IN A RADIOFREQUENCY INDUCTIVELY COUPLED PLASMA

GEORGE F. LARSON and VELMER A. FASSEL

Anal. Chem. 48: 1161 (1976)

Abstract--The results of a comparative study on the extent to which various interelement or interference effects are observed in a microwave-excited, single-electrode plasma (SEP) and a radiofrequency-excited, inductively coupled plasma (ICP) are presented. These studies confirmed earlier reports that easily ionizable elements generally produce severe changes on the line emission of analyte elements in the SEP, whereas only negligible or small effects are observed in the ICP. It is also shown that several concomitants with differing ionization potentials produce significant changes in the emission intensity of Mo in the SEP although only small effects are observed in the ICP and that PO_4^{3-} or Al^{3+} concomitants produce significant interference on calcium atomic and ionic line emission in the SEP while negligible effects are observed in the ICP.

ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS OF COAL

E. L. DeKALB and V. A. FASSEL

Proc. ERDA X- and Gamma-Ray Symposium, Ann Arbor, Michigan, May 19-21 (1976)

Abstract--The x-ray fluorescence determination of sulfur and other constituents in coal ordinarily requires correction for a variety of interelement effects, which can be troublesome and time consuming. For mineral specimens with 6 to 10 major constituent elements, a large number of well characterized samples or synthetic standards are required to establish appropriate correction factors when bulk samples are analyzed.

However, when the sample is prepared as a thin film specimen by the Chung procedure, interelement corrections can be neglected, and only a few samples which have been analyzed previously for the elements of interest are needed for calibration. The adaptation of the Chung method of sample preparation to coal samples will be described and illustrated in detail. Precision and accuracy data for the determination of sulfur in thin-film coal samples are presented.

OSTEOGENIC SARCOMA: INFLUENCE OF TRACE METALS IN
EXPERIMENTAL INDUCTION

Joseph M. Janes, John T. McCall and RICHARD N. KNISELEY
Mayo Clinic Proc. 51: 433 (1976)

Abstract--The experimental induction of osteogenic sarcoma in rabbit bone by zinc beryllium silicate has been under study for 25 years. In experimental animals and in humans with osteogenic sarcoma, analysis showed differences in the contents of trace metals between normal bone and tumor. Phosphors obtained during the early stages of the study were tumor-igenic, whereas those obtained later were not. Analysis of the different phosphors indicated differences in contamination by the trace metal. These differences would seem to be important in tumorigenesis.

THE HIGH TEMPERATURE VAPORIZATION OF DEFECT SCANDIUM
MONOSULFIDE

R. T. TUENGE, F. LAABS, and H. F. FRANZEN
J. Chem. Phys. 65: 2400 (1976)

For Abstract see I. High Temperature Chemistry, page 88.

II. ANALYTICAL SEPARATIONS

SEPARATION OF METAL IONS USING A HEXYL THIOGLYCOLATE RESIN

ELIZABETH M. MOYERS and JAMES S. FRITZ

Anal. Chem. 48: 1117 (1976)

Abstract--The synthesis, characterization and some analytical applications of a new chelating resin are described. The new resin, HTG-4, is synthesized from a highly cross-linked, macroporous resin (XAD-4) and contains the hexylthioglycolate functional group. HTG-4 is highly selective for silver(I), mercury(II), bismuth(III), and gold(III) in acidic-aqueous solution. The first three metal ions are sequentially eluted with 0.5 to 6 M hydrochloric acid, and gold(III) is eluted with a thiourea solution. Several quantitative analytical separations are reported.

CONCENTRATION AND SEPARATION OF TRACE METALS WITH AN ARSONIC ACID RESIN

JAMES S. FRITZ and ELIZABETH M. MOYERS

Talanta 23: 590 (1976)

Abstract--A series of macroporous arsonic acid resins has now been prepared by a synthetic method similar to that used by Hirsch et al. The effect of varying pore diameter and surface area on the properties of the final resins has been studied. These arsonic acid resins are now proposed for the concentration of trace metal ions from hard water and sea-water.

COPPER(II) SALTS AS AMINE ABSTRACTORS IN GAS CHROMATOGRAPHY

COLIN D. CHRISWELL, LARRY D. KISSINGER, and JAMES S. FRITZ

Anal. Chem. 48: 1123 (1976)

Abstract--An effective amine abstractor for use in gas chromatography was prepared by coating Chromosorb G AW/DMCS with copper(II) chloride. Other abstractor materials prepared were less effective. Pre-columns

containing copper(II) chloride coated Chromosorb G retained all amines tested and had negligible effects on the separation of other types of compounds on analytical columns. Attractive properties of amine abstractors were demonstrated by separating pyridine solutions of alcohols, ketones, halogenated hydrocarbons, alkanes, alkenes, and aromatic hydrocarbons on appropriate analytical columns with and without the use of amine abstractor precolumns. Applications of the abstractor were demonstrated in methods for determining volatile components in coal, on modifications of the resin sorption method for determining part-per-billion concentrations of organic impurities in water, and for determining impurities in reagent grade pyridine.

REMOVAL OF COPPER AND IRON PRIOR TO WATER HARDNESS TITRATION

JAMES S. FRITZ and JEFFREY N. KING

Anal. Chem. 48: 570 (1976)

Abstract--Silica gel was reacted with 3-aminopropyltriethoxysilane or with the N-methyl derivative of the same reagent to produce a material with an amino silyl functional group. If a water sample in the pH range of 5.0 to 7.5 is passed through a short column of this material, iron(II) and copper(II) are completely retained, while calcium(II) and magnesium(II) pass through. This permits an accurate water hardness titration without adding any cyanide.

SIMPLIFIED RESIN SORPTION FOR MEASURING SELECTED CONTAMINANTS

G. A. JUNK, J. J. RICHARD, H. J. SVEC, and J. S. FRITZ

J. Am. Water Works Assn. 68: 218 (1976)

Abstract--In an extensive study initiated at Iowa State Univ. the concentrations of three pesticides--atrazine, DDE, and dieldrin--in various

surface, subsurface, and finished waters were measured. Surface water from every major watershed in Iowa was found to have appreciable levels of contamination, with seasonal and climatic fluctuations that were consistent with an agricultural runoff model. Waters from shallow wells and from water-treatment plants were also contaminated. The contamination was either not detected or found at < 1 ng/l in water from deep wells located outside the alluvial plain of contaminated rivers. Water-treatment processes, even charcoal-bed filtration, employed at one modern treatment plant, were shown to be ineffective in reducing the pesticide concentration. Other applications and tests of the resin-sorption method for monitoring organic contaminants are presented herein.

This work supported in part by NSF.

ANALYSIS OF DRINKING WATER FOR HALOFORMS

LARRY D. KISSINGER AND JAMES S. FRITZ

J. Am. Water Works Assn. 68: (August 1976)

Abstract--Storage of water samples has often produced an increase in haloforms as chlorine compounds reacted with substances in the water; the addition of ascorbic acid stabilizes the samples for eventual determination of their composition.

This work supported in part by NSF.

III. ANALYTICAL MASS SPECTROSCOPY

APPLICATIONS OF RESINS FOR EXTRACTING ORGANIC COMPONENTS FROM WATER

G.A. JUNK, C. D. CHRISWELL, R. C. CHANG, L. D. KISSINGER,
J. J. RICHARD, J. S. FRITZ, and H. J. SVEC
Z. Anal. Chem. 282: 331 (1976)

Abstract--The discussion of the applications is prefaced by very brief descriptions of 1) the resin characteristics, 2) the extraction device, 3) some efficiency tests, and 4) the general methodology. Recent developments of simple and inexpensive procedures for the monitoring of selected contaminants of concern are stressed. Examples are given of the contamination of water by PVC tubes and of the measurements of pesticides, amines, halocarbons, and model compounds in water. Practical comparisons of the resin sorption method to carbon sorption and solvent extraction procedures are presented and recently developed mini-samples are discussed.

This work was supported in part by NSF.

AN AUTOMATIC ELECTROMETER RANGING CIRCUIT FOR A SPARK-SOURCE MASS-SPECTROMETER

R. J. CONZEMIUS and G. A. SLEEGER
Talanta 23: 556 (1976)

Abstract--Electrical measurements of ion-current signals from spark-source mass-spectrometers present unique experimental difficulties. One of these is the automatic ranging of a sensitive electrometer amplifier during the sequential measurement of different ion-signals by peak-switching techniques. These ion-signals, which commonly fluctuate between zero and high current, are too erratic for commercial auto-rangers. This paper describes briefly an electronic circuit which satisfactorily performs automatic attenuation on a Cary 401 MR electrometer used for measuring spark-source

mass spectrometer ion-signals. The general electrical detection system has already been described.

MICROPHOTOMETER MODIFICATION FOR AUTOMATIC RECORDING OF
SPARK SOURCE MASS SPECTRA

R. J. CONZEMIUS, D. J. ADDUCI, G. O. FOSS, and H. J. SVEC

Anal. Chem. 48: 1647 (1976)

Abstract--Computer based schemes for interpreting mass spectra require accurate input of intensity and mass. When the spectra are recorded on a photographic plate and remote large centralized computers are available for handling complex interpretive programs, it becomes desirable to get the pertinent spectral information (i.e., line transmittance, background, line location, and exposure) quickly and accurately to the computer. This paper describes a moderately low cost modification to a commercial microphotometer which permits automatic measurement of spectral line position, exposure, and transmittance on spark source mass spectrometer photoplates. Spectral lines are located and scanning functions are controlled manually. Measured data and operator input are displayed visually and stored with a remote video terminal. The stored information is transferred subsequently via the telephone lines to a large central computer for data processing.

The system described here has a number of advantages over other reported systems. First, an on-line computer is not required. Instead, the advantages of a large centralized computer such as large area data storage, high level program coding, shared costs of maintaining and upgrading the computer are used. Second, costs are kept low by making minimal modifications to a commercial microphotometer and by utilizing conventional electronic

circuitry for data reading and transfer control. Third, the system is relatively fast. A photoplate containing 300 lines can be read in ~ 40 minutes. The system reads accurately at scan rates of up to 25 mm/min and easily keeps up with manual rates required for line location and scan control functions. Fourth, the system is not dependent upon reproducibility of scan rates. Fifth, maximum use is made of operator capability for decisions without the burden of actual data recording.

RESIN SORPTION METHODS FOR MONITORING SELECTED CONTAMINANTS IN WATER

GREGOR A. JUNK, JOHN J. RICHARD, JAMES S. FRITZ, and HARRY J. SVEC
Identification and Analysis of Organic Pollutants in Water, ed. L. H. Keith
 (Ann Arbor, Michigan: Ann Arbor Science Press, 1976) pp. 135-153.

Abstract--Applications of XAD-2 resin sorption methods for the convenient monitoring of selected lipophilic contaminants in water are discussed. In one extensive study the concentrations of three pesticides, atrazine, DDE, and dieldrin, in various surface, sub-surface and finished waters were measured. The amounts ranged from several micrograms to less than one nanogram per liter (ng/l) of water. Surface water from every major watershed in the State of Iowa (U.S.A.) had appreciable levels of contamination with seasonal and climatic fluctuations which were consistent with an agricultural runoff model. Waters from shallow wells and from water treatment plants were also contaminated. The contamination was either not detected or found at less than one ng/l in water from deep wells located outside the alluvial plain of contaminated rivers. Water treatment processes, even charcoal bed filtration as employed at one modern treatment plant, were shown to be ineffective in reducing the pesticide concentration. Other applications and

tests of the resin sorption method for monitoring selected organic contaminants are presented.

This work was supported in part by National Science Foundation.

SIMPLIFIED RESIN SORPTION FOR MEASURING SELECTED CONTAMINANTS

G. A. JUNK, J. J. RICHARD, H. J. SVEC and J. S. FRITZ

J. Am. Water Works Assn. 68: 218 (1976)

For abstract see II. Analytical Separations page 129.

AN ARC FLOATING ZONE TECHNIQUE FOR PREPARING SINGLE CRYSTAL LANTHANUM HEXABORIDE

J. D. VERHOEVEN, E. D. GIBSON, M. A. NOACK and R. J. CONZEMIUS

J. Crystal Growth 36: 115 (1976)

For abstract see Physical Properties, page 36.

IV. LASERS IN ANALYTICAL CHEMISTRY

THEORY OF PURE ROTATIONAL RAMAN TRANSITIONS IN THE VIBRONIC GROUND STATE OF A TETRAHEDRAL MOLECULE

ARIEH ROSENBERG and KUO-MEI CHEN

J. Chem. Phys. 64: 5304 (1976)

Abstract--It is well known that the polarizability tensor of a rigid tetrahedral rotor is isotropic. Hence, pure rotational Raman transitions in the vibronic ground state of a tetrahedral molecule are forbidden. However, the distortion of the molecule by centrifugal forces produces an effective anisotropic polarizability tensor, which depends on the components of the total angular momentum, and results in a pure rotational Raman spectrum. The purpose of this Communication is to give explicit expressions for the polarizability tensor operator and the scattering intensity of the pure rotational Raman transitions. The feasibility of observing such transitions and an estimate of the relative intensity are given for the case of methane. The results presented here have been derived partially by considering the matrix elements of the

linear normal coordinate terms in the polarizability tensor, between perturbed wavefunctions that were obtained by mixing the ground state with the degenerate excited vibrational states. The existence of similar "forbidden" pure rotational transitions in the far infrared region were established recently both on theoretical and experimental grounds.

APPLICATION OF INTERFEROMETRY TO SIMULTANEOUS MULTIELEMENT
ATOMIC EMISSION SPECTROMETRY

RICHARD PRUIKSMA, JAMES ZIEMER, and EDWARD S. YEUNG
Anal. Chem. 48: 667 (1976)

Abstract--A technique for simultaneous multielement analysis based on a scanning Fabry-Perot interferometer and atomic emission is described. Detection limits are determined for various common elements using the oxygen-hydrogen flame as a test case. The results show that semitrace to trace levels in solution can be analyzed. This technique is limited to groups of elements which contain relatively few total emission lines in a certain wavelength region. Spectral interference can, in general, be eliminated by the proper choice of the interferometer spacing. Analysis of tap water and parameters essential to this optical scheme are discussed. The main advantages of this technique are the high luminosity and the ability to perform analysis in the millisecond time scale.

ATOMIC FLUORESCENCE SPECTROMETRY USING A FLASHLAMP-PUMPED
DYE LASER

HERBERT L. BROD and EDWARD S. YEUNG
Anal. Chem. 48: 344 (1976)

Abstract--A detailed theoretical analysis of signals in atomic fluorescence, including the effects of pre-absorption under saturation conditions, is presented. These predictions are compared with experimental measurements.

using a flashlamp-pumped dye laser. A detection limit of $7 \times 10^{-15} \text{ g/cm}^3$ of sodium is obtained using a simple arrangement. The calibration curves compare well with theory with no adjustable parameters. The wavelength dependence and the time dependence of the signals are also discussed. We suggest that peak intensity measurements are more reliable than integrated intensity measurements for analytical purposes.

EMISSION RATE OF A MULTILEVEL ATOM AND ITS QUANTUM BEATS

I. C. KHOO and H. J. Eberly

Phys. Rev. A 14: 2174 (1976)

Abstract--Using the Heisenberg operator approach, we have calculated the emission rate of a multilevel atom whose transitions involve both upper- and lower-state splittings. The emission rate is first calculated by a frequently used power-flow expression and is shown to exhibit lower-state beats. This power-flow expression requires care in its interpretation because it does not account for the measurement process. We then derive an alternative, detection-oriented emission rate and show that lower-state beats are not observable in a photodetection experiment.

COLLISION-INDUCED ABSORPTION OF GASEOUS SILANE IN THE FAR INFRARED

ARIEH ROSENBERG and Irving Ozier

J. Chem. Phys. 65: 418 (1976)

Abstract--The collision-induced spectrum of SiH_4 has been studied between 32 and 400 cm^{-1} with a Michelson interferometer. From a band shape analysis and a spectral moment calculation, it is concluded that the octopole moment Ω dominates the induction process, but that current treatments of octopolar induction cannot completely account for the data. Either

these treatments are incomplete in some way, or a second induction mechanism makes a significant contribution to the absorption. If the discrepancies are attributed to a hexadecapole moment Φ , then it is found that $|\Omega| = (2.6 \pm 0.3) \times 10^{-34}$ esu cm³ and $|\Phi| = (5.9 \pm 1.9) \times 10^{-42}$ esu cm³. An algebraic error in the symmetrized calculation of Ozier and Fox (1970) is corrected and the minor changes in the spectra due to the correction are discussed.

V. ATMOSPHERIC POLLUTION MONITORING BY DIODE LASERS

PRESSURE-BROADENED LINEWIDTHS OF NITRIC OXIDE

G. D. T. TEJWANI, BRUCE M. GOLDEN, and EDWARD S. YEUNG
J. Chem. Phys. 65: 5110 (1976)

Abstract--N₂-broadened linewidths of NO in the 5.4 μ band have been measured. This provides a means of determining the quadrupole moment of NO, which has been poorly measured so far. Using the Anderson-Tsao-Curnutte theory of line broadening, and this new value, 2.4×10^{-26} esu.cm², for the quadrupole moment of NO, self-broadened and foreign-gas (N₂ and O₂)-broadened linewidths of NO at 300 K for all important infrared transitions are calculated. In the self-broadening calculations, dipole-dipole, dipole-quadrupole, quadrupole-dipole, quadrupole-quadrupole, induced, and dispersion interactions were taken into account. For the case of foreign-gas broadening, dipole-quadrupole, quadrupole-quadrupole, dipole-hexadecapole, quadrupole-hexadecapole, induced and dispersion interactions were considered. Air-broadened linewidths of NO have also been computed at 200, 250 and 300 K.

MATHEMATICAL AND COMPUTER SCIENCES

Mathematical Sciences

THE NEED FOR A NEW CLASSIFICATION OF DOUBLE HYPERGEOMETRIC SERIES

B. C. CARLSON

Proc. Am. Math. Soc. 56: 221 (1976)

Abstract--An elementary proof is given of a linear transformation which changes a particular double hypergeometric series of order two into a series of order three. A similar transformation holds for a particular series of arbitrary order in two or more variables. The change in order provides new evidence, the most compelling to date, that the order of such a series is not a fundamental property. This conclusion undermines the accepted classification of hypergeometric series in more than one variable.

QUADRATIC TRANSFORMATION OF APPELL FUNCTIONS

B. C. CARLSON

SIAM J. Math. Anal. 7: 291 (1976)

Abstract--A double integral average of X^t with two rows and two columns has eight quadratic transformations into itself, each with two free parameters and two independent variables. Three of the transformations change double hypergeometric series of order two into series of order three, and one of these (modified by a linear transformation applicable to polynomial cases) permits a very direct proof of the addition theorem and related results for Gegenbauer polynomials. Two others transform Appell's F_2 into F_2 or F_1 , and two transform F_1 into F_1 . One of the latter contains Landen's transformation of the first and second incomplete elliptic integrals, and the other contains Bartky's transformation of the third complete elliptic integral.

A SINGULAR INTEGRAL EQUATION: Solution

B. C. CARLSON

SIAM Rev. 18: 494 (1976)

Abstract--The singular integral equation

$$Z(s) = \lambda \int_0^1 Z(t) (1 - st)^{-1} dt$$

occurs in the thermodynamics of a one-dimensional spin system. It is proved that the spectrum of eigenvalues covers the open right half-plane.

The solution corresponding to $\lambda = (\sin \pi a)/\pi$, $0 < \text{Re } a < 1$, is

$$Z(s) = (1-s)^{a-1} {}_2F_1(a, a; 1; s).$$

Computer SciencesSUBSPACE SELECTION ALGORITHMS TO BE USED WITH THE NONLINEAR PROJECTION METHODS IN SOLVING SYSTEMS OF NONLINEAR EQUATIONS

D. D. GEORGE and R. F. KELLER

Comp. & Maths. with Appls. 2: 225 (1976)

Abstract--The nonlinear projection method are minimization procedures for solving systems of nonlinear equations. They permit reevaluation of $\underline{n}_k$, $1 \leq \underline{n}_k \leq \underline{n}$, components of the approximate solution vector at each iteration step where $\underline{n}$ is the dimension of the system. At iteration step $\underline{k}$, the reduction in the norm of the residue vector depends upon the $\underline{n}_k$ components which are reevaluated. These $\underline{n}_k$ components are obtained by solving a linear system.

We present two algorithms for determining the components to be modified at each iteration of the nonlinear projection method and compare the use of these algorithms to Newton's method. The computational examples demonstrate that Newton's method, which reevaluates all components of the

approximate solution vector at each iteration, can be accelerated by using the projection techniques.

ENVIRONMENTAL RESEARCH AND DEVELOPMENT

Environmental Studies

ENVIRONMENTAL EFFECTS OF ENERGY RELATED PROCESSES AND POLLUTANTS IN THE ENVIRONMENT

The following article was done as combined research with an Ames Laboratory
subcontractor--Montana State University

BIOLOGICAL FEASIBILITY OF SITING COAL FIRED POWER PLANTS AT COLSTRIP, MONTANA

C. C. GORDON

Western Wild lands 2: 28 (1976)

Abstract not available.

PHYSICAL AND TECHNOLOGICAL STUDIES

Characterization, Measurement and Monitoring

X-RAY EXCITED OPTICAL LUMINESCENCE OF POLYNUCLEAR AROMATIC HYDROCARBONS

A. P. D'SILVA, G. J. OESTREICH and V. A. FASSEL

Anal. Chem. 48: 915 (1976)

Abstract--The x-ray excited optical luminescence of polynuclear aromatic hydrocarbons (PAH) dissolved in Shpol'skii solvents and frozen at 90 K. has been observed for the first time. The limits of detection for the compounds that give the most intense spectra, e.g., perylene, 3-4 benzopyrene and coronene are shown to be at nanogram levels.

NUCLEAR RESEARCH AND APPLICATIONS

Technology Development and Special Projects

CONVERSION TECHNOLOGY

THE PREPARATION OF GADOLINIUM METAL FOR THERMOELECTRIC DEVICES

B. J. BEAUDRY, P. E. PALMER and K. A. Gschneidner, Jr.
Proceedings of the 11th Intersociety Energy Conversion Engineering Conference (New York: American Institute of Chemical Engineers, 1976) pp. 1556-1560.

Abstract--The procedure used to prepare high purity gadolinium in 100 to 250 g quantities at the Ames Laboratory is described. The important differences between the Ames Laboratory procedure and the large scale industrial processes and how these affect the purity of the gadolinium is discussed.

A method was developed for producing kilogram quantities in the same purity as the metal produced on the small scale. The new procedure eliminates the costly distillation step by a simple change of crucible and proper heat cycle.

The gadolinium is used as small pellets to prepare Gd_2Se_3 . The special arc melting hearth which was designed and built to facilitate the preparation of these pellets in large quantity are described.

A STUDY OF THE PURIFICATION OF Gd BY ELECTROREFINING

HIROSHI NAGAI, B. J. BEAUDRY and K. A. GSCHNEIDNER, Jr.
12th Rare Earth Research Conference (Denver, Colorado: University of Denver, 1976) Vol. I., pp. 470-479.

Abstract--Gadolinium metal can be prepared 99.98% pure by the calcium reduction of GdF_3 if (1) the reactants are highly purified, (2) the reactants and products are handled under inert conditions, and (3) the metal is

vacuum melted at high temperatures followed by distillation. Since the process is costly in time and materials, an alternate method which would involve the electro-purification of crude gadolinium was studied.

The electrolyte studied was $\text{LiCl} : \text{LiF} : \text{GdF}_3$. The best results were obtained with a 77.6 wt.% LiCl , 11.2 wt.% LiF , 11.2 wt.% GdF_3 electrolyte at 700°C . It was shown that the purity of the deposit was strongly dependent on the purity of the electrolyte and the temperature. The purest deposit of Gd was obtained when the LiCl and LiF were purified by distillation and high purity GdF_3 was used. The effect of various methods used to remove the adhering electrolyte salts and to consolidate the deposited dendrites was studied. Removal of the adhering salts by distillation followed by arc melting of the dendrites gave the purest Gd . The analyses of the metal prepared under the various conditions are given.

PUBLICATIONS BY NON-SALARIED ASSOCIATES OF THE AMES LABORATORY

CONJUGATED CIRCUITS AND RESONANCE ENERGIES OF BENZENOID HYDROCARBONS

Milan Randić

Chem. Phys. Lett. 38: 68 (1976)

Abstract--A concept of conjugated circuits contained in Kekulé forms of benzenoid hydrocarbons is considered. Circuits of size $(4n + 2)$ in which CC single and double bonds formally alternate are enumerated and serve as the basis for the characterization of a given system. Resonance energies of benzenoid systems are given by contributions of conjugated circuits of different size. The scheme permits the expression of resonance energies of different molecules in terms of selected reference compounds, such as linear acenes. The approach is illustrated on a dozen benzenoid hydrocarbons and the calculated resonance energies are on average within 0.05 eV of the values obtained by SCF MO calculations.

ON DISCERNING SYMMETRY PROPERTIES OF GRAPHS

Milan Randić

Chem. Phys. Lett. 42: 283 (1976)

Abstract--A procedure is outlined which allows the symmetry properties of graphs to be systematically and rigorously investigated. It is based on a search for all the automorphisms of a graph and this is accomplished by suitably applying the procedure for recognizing identical graphs. It consists of finding all the distinctive labeling of the vertices of graph associated with the smallest binary code derived by a particular interpretation of the associated adjacency matrix. No prior cognizance of symmetry operations is required

which is in contrast to the usual discussions of the symmetry properties of molecules which are based on the knowledge of pertinent symmetry operations. This is important since in graphs it is neither apparent nor generally possible to simply enlist those permutations of labels which leave the connectivity invariant (i.e., do not alter the form of the adjacency matrix). The procedure is applied to the Petersen graphs and the Desargues-Levi graph, both associated with isomerizations of trigonal bipyramidal complex and other chemical transformations. It is shown that these graphs of high symmetry belong to symmetry groups of order 120 and 240 respectively. The approach can also provide a basis for the development of the symmetry properties of non-rigid molecules in which connectivity is preserved.

LOW-LEVEL STABILITY AND POLLUTANT-TRAPPING POTENTIAL FOR A RURAL AREA

E. S. Takle, R. H. Shaw and H. C. Vaughan
J. Appl. Meteorology 15: 36 (1976)

Abstract--Temperature and wind speed measurements over a 6-year period from a 32 m tower located in a primarily rural area are used to assess the pollutant-dispersive characteristics of a rural site. A monthly comparison of a crude pollution-trapping index shows July through September the most favorable, and December through February the least favorable, months for the trapping of contaminants emitted from ground-based sources in rural areas.

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