RECEIVED BY DTIC NOV 12 1970

C00-623-156

MASTER

SOLID STATE PHYSICS PROGRAM

ANNUAL PROGRESS REPORT

ATOMIC ENERGY COMMISSION

CONTRACT NO. AT (11-1)-623

NOVEMBER, 1970

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CASE WESTERN RESERVE UNIVERSITY

UNIVERSITY CIRCLE

CLEVELAND, OHIO 44106

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

INTRODUCTION

During the period from November, 1969, through October, 1970 seven Technical Reports have been issued. These reports are the research product of our students, research associates and faculty and are listed in Appendix II. In the same period twenty-two papers were in the publication stage as shown in Appendix III; some of these are later versions of Technical Reports and others represent the independent work of the faculty. The body of this report describes chiefly work that is still in progress, or work that has not yet been written up for a Technical Report. Details of finished work are to be found in the accompanying copies of the Technical Reports, preprints and reprints. Appendix I lists the personnel associated with the project. Four of the graduate students joined the project and six have left. We are listing in the category Graduate Summer Students first year graduate students who are making a contribution to our research but generally supported by the University. There were also four undergraduate students who carried out research as part of their senior year program. Dr. George Juras is with us as a Research Associate for a second year. Professor Schuele is on leave at the Bell Telephone Laboratories, Columbus, effective September, 1970.

In addition to the research activities of our faculty described in this report, we also call attention to these contributions. Professor Taylor's graduate level text "A Quantum Approach to the Solid State" was published by Prentice Hall. Professors Schuele and Hoffman are editing Critical Reviews in Solid State Sciences, one of the

new quarterly Chemical Rubber Company review journals. Professor Hoffman, together with Dr. M. H. Francombe of the Westinghouse Research Laboratories, is also editor of Volumes 6 and 7 of "Physics of Thin Films" published by Academic Press.

The body of this report is grouped into three areas: (A) Thin Film Physics; (B) Cohesive Properties of Crystals; and (C) Solid State Theory. The Thin Film Physics Program is directed by Professor Hoffman. The UHV Mössbauer measurements and their contemplated application to surface measurements and nuclear reaction are growth problems and were an important progress of the past year. The additional structural information obtained from high voltage electron microscopy is proving of value in understanding the origin of the internal stresses. Professor Schuele's program in cohesive properties has compiled an amazing amount of highly accurate data for the dielectric constants and their pressure derivatives of ionic crystals. These data are so reliable that a secondary standard for high pressure gages has been very active. The magnetoresistance and size effects in metals as well as the continuation of the virtual recoil effects calculations are especially pointed out.

All the faculty associated with this project have spent approximately 50% of their effort on the research described during the academic year, and 100% of their effort for two summer months. With the exception of Professor Schuele, who started a leave of absence 1 September, 1970, they will continue to spend half of their time on this research.

A. THIN FILM PHYSICS

1. Torque Magnetometer Measurements - R. E. Chase and R. W. Hoffman.

The work with Ni on films thicker than $25\text{\AA}$ has now been published [J. Appl. Phys. 41 1623 (1970)] and is appended as COO-623-132. This work sets limits on the applicability of the single domain model to thin film magnetics.

Our goal of obtaining data has not been met owing to difficulties in the servosystem in measuring the small torques expected from oligatonic films. Much of this past year was spent putting the magnetic measurement instrumentation into working order. The servosystem was almost completely rebuilt. Modifications include a new DC servomotor, a simplified gear train, a new servoamplifier, a more sensitive sample position detector, and more stable power supplies for the position detector lamp and damping magnet.

During the past year we have converted space into a semi-clean room for preparation of UHV samples. Facilities include filtered air conditioning, a laminar flow bench with a KEPA water deionizer and plumbed-in nitrogen drying gas.

2. Mössbauer Measurements - A. C. Zuppero, M. N. Varma and R. W. Hoffman.

The preliminary measurements have been published in J. Vac. Sci. Tech. 7, 118 (1970) and reprints are appended. Technical Report No. 62 has been issued and describes the completed experiment on films

made in UHV and measured at ambient pressure. The abstract of the technical report follows:

The properties of ultra thin films of iron have been studied in air using the Mössbauer technique. The surface density of atoms ranged from 10^{13} to 10^{18} atoms/cm². This range corresponds to atomic situations in which 99% of the substrate is empty to the situation where bulk properties have been observed by methods in addition to our own. The method of analysis requires that some of the atoms of the film emit information about their atomic surroundings, in contrast to the usual Mössbauer absorption spectroscopy.

The analyzer system utilized an asymmetric triangle as the velocity relation between source and absorber, which simplified the analysis by not requiring folding of data before observation. A computer CRT interface was used in the computation of spectrum parameters using optical first estimates and thus greatly reduced computation divergences.

The results of the thinnest film seem to indicate that the bonding is that of atoms on a surface and that the type of site occupied by any film atom is equivalent to that occupied by any other. As the surface density of atoms is increased a broad, almost featureless resonance appears, and this spectrum may be observed to surface densities up to the order of 10^{17} atoms/cm² and to temperatures as low as 5°K. In one sample part of the feature-free spectrum was converted to that spectrum characteristic of stable magnetic behavior by application of small magnetic fields and in

others by cooling to liquid nitrogen temperatures. This may indicate that part of the thicker films consisted of clusters of the correct size to be switched to stable magnetic behavior, as predicted in the theory of superparamagnetism. The thickest films exhibited either the bulk value of internal magnetic fields within 20% or non-magnetic spectrum. The latter is interpreted as possibly a new form of iron or iron-oxide.

The new UHV Mössbauer spectrometer referred to in last year's proposal was completed in good time. The Varian ultra high vacuum system and a variable temperature dewar from Janis research were received in June 1969, and the counter and Mössbauer drive was constructed and installed on the system. In October 1969 the first film was evaporated inside the UHV system and analyzed. The computer program Grasp and Action were modified to fit the Mössbauer data. In January 1970 a temperature controller was built and a germanium sensor was installed on to the neck of the dewar. The temperature of the block is controllable to 0.1°K. Significant data has been obtained and analyzed, but we must interpret the spectra obtained in a detailed way. Thickness measurement of the samples by radioactive method has also been obtained. Results of the preliminary measurements have been submitted to the Journal of Applied Physics and will be presented at the November Magnetism and Magnetic Materials Conference.

The abstract of this paper follows:

Mössbauer emission spectra are used to determine relaxation effects of $\text{Fe}^{57\text{m}}$ in thin iron films deposited at 10^{-9} Torr and measured at 10^{-11} Torr. The spectra from the radioactive films

have been analysed at room temperature, liquid nitrogen and 15°K over a range of thickness from 3×10^{16} atoms/cm² to 0.12×10^{16} atoms/cm² (25 Å to 1 Å). Samples thinner than 7 Å show the following characteristics: a positively resolved doublet interpreted as quadrupole splitting of about 0.6 mm/sec. independent of thickness and temperature; a Mössbauer fraction roughly constant with temperature; one line increases in width and area and the other decreases as the temperature is lowered. Samples thicker than 10 Å are approximately characteristic of bulk iron. The transition is ascribed to superparamagnetic fluctuations in the internal field but the detailed line shapes are not simply explained. A multilayer 25 Å sample has six lines in the normal positions at 15 and 80°K, but the outer lines show a decreasing intensity as the temperature increases until they vanish at room temperature.

3. Stress in Platinum Films - R. E. Rottmayer and R. W. Hoffman.

Reprints are appended for the note on the elastic boundary conditions for cantilevered beams used in the stress measurements that was published in J. Vac. Sci. Tech. 7, 461, (1970).

The measurements and interpretation of the temperature dependence of the intrinsic stress in platinum have now been reported in Technical Report No. 64, whose abstract follows. An abridged version will be presented at the Washington AVS Meeting in October and has already been accepted for publication in J. Vac. Sci. Tech.

A detailed analysis of the cantilevered beam technique for measuring stress in thin films has been performed. The limits of

applicability of the derived equations have been defined with respect to large deflections, shear distributions at the edge of the substrate and boundary conditions at the clamp.

The stress in platinum thin films has been measured on glass and single crystal silicon substrates as a function of thickness with substrate temperatures ranging from 100°C to 600°C. The stress was found to have a high tensile value at low temperatures, to decrease sharply at 300°C and to be very small at 500°C and 600°C.

At 1 MeV microscope enabled very thick (1300A) films to be examined. Their growth was found to be columnar at 100°C and 300°C with grains of average lateral extent, 100A. At 600°C the small 100A grains grew together and formed large grains, 1000A in lateral extent.

A comprehensive theory based on the structural observations was proposed. The high tension at 100°C was explained by the interaction at the grain boundaries. The decrease in stress at 300°C was ascribed to diffusion in the growing film. The small stress at 500°C and 600°C was the result of a larger grain size.

4. Stress Anisotropy - F. A. Doljack and R. W. Hoffman

The thermal deposition of nickel on circular fused quartz substrates which approximate "free" boundary conditions resulted in an unacceptable stress measurement due mainly to the inability to control substrate temperature over the range of temperatures in which the stress exists. Consequently, the problem of the deflection of a thin circular plate with a uniform biaxial surface traction and rigidly

clamped along an inner circumference was solved. The new experimental design consists of 5 mil thick, polished [111] silicon disks center - clamped to a circular, cylindrical OFHC copper clamp which is positioned through a center hole in a quartz optical flat. The flat is used to produce the interference fringes for the deflection measurement. The temperature of the copper clamp is controllable from 25°C to over 700°C. The high thermal conductivity of the silicon should keep temperature differences across the substrate during deposition to less than 2°C in the worst case. Some difficulty is being experienced in the cracking of the thin silicon substrates because of differential thermal expansion.

Preliminary high voltage microscopy was done at the U. S. Steel laboratory and is being continued with the completed installation of the 650 KV Hitachi microscope on our campus. Electron microscopy of 1000 Å thick nickel samples grown on carbon substrates showed the occurrence of large single crystals among the typical 100 Å size particles for films grown at temperatures somewhere above 100°C. A 2500 Å thick film grown at 25°C showed only 100 Å size particles when studied with the 650 KV electron microscope.

5. Magnetic Measurements - R. Springer and R. W. Hoffman.

A simple, but relatively accurate method for measuring the bulk magnetization of thin films was developed in 1946 by this laboratory. The apparatus is designed to measure samples that are long, narrow and thin. (4 cm x .5 cm x 100 Å).

A re-design and improvements have been made to achieve a higher performance instrument. The apparatus consists of two long solenoids that are used to provide a uniform axial field. They are capable of reaching fields of 1000 gauss peak to peak. The voltage source is the standard 60 Hz line. The actual construction of these coils is two lucite pipes that are co-axial and sealed together at the ends for forms. Their transformer oil may be pumped through them to cool the windings. Care was taken in choosing the gauge of wire, and insulating material between layers. It was found that without much trouble, low frequency ringing can occur in these windings and that signal detected in the pickup winding.

Inside the center of the coil forms are the pickup coils. They are connected in such a manner that any common mode signal is rejected. Each coil is wound in four clumps consisting of 2500 turns each. Thus 10,000 turns gives good sensitivity. Lumping of the windings is necessary and keep this resonance high ($\sim 16K$ Hz). One coil remains fixed, the other is moveable.

The moveable mechanism must be completely free from slip stick and must not contain any magnetic parts. Ways of lucite were machined and a phenolic slider used. The electronics necessary is a low noise pre-amp of gain ~ 1000 , an integrator, and an x-y oscilloscope. The low noise pre-amp was a current sourced differential pair input with low bias currents. The common mode rejection is ratio ~ 67 db, noise $\sim 5\mu V$, input impedance $\sim 140K \Omega$ and band width .25 Hz-100 Kc. The integrator is a variable gain active type. The

design of this is straight forward.

The signal from the pickup coils is fed into the low noise pre-amp through the integrator and to the scope. The horizontal section derives its signal from a resistor that senses the current in the main solenoids. This current is directly proportional to the driving fields.

When the currents are turned on, a signal from the pickup coils may be observed on the scope face without a sample. The character of the signal takes two forms. One is a tilting of the integrated signal, and the other is an opening. The opening is caused by eddy current losses in the winding of the solenoids and cross coupling effects. The tilt is caused by the fact that the emf, due to the main fields, developed at the pickup coils is not the same. These two problems are easily remedied. The first is compensated by the use of one moveable shorting turn on the main solenoid. When this moved up and down the length proper bucking of the opening is achieved. The tilt can be remedied by changing the location of one pickup coil in the solenoid. This is why a non-slip stick method of travel is important, as movements of only a few thousands of an inch are required.

When the bucking has been achieved, then the sample may be introduced into the sample pickup coil and the M-H loop observed.

6. Liquid Crystal Thermography - J. Strok and R. W. Hoffman.

The determination of the temperature distribution in a thin substrate is a difficult task both theoretically and experimentally.

This problem is of interest since circular substrates are used to measure the internal stresses, and we must correct for differential thermal expansion effects. A technique was developed to determine the isotherm using liquid crystals by Jack Strok, a Case Institute Senior Physics major. The results of the temperature profile of a mockup of the earlier stress apparatus are:

The isotherms of two circular glass disks $1/2$ " in diameter, $6.5 \pm .1$ mils thick, and separated by a $1 \pm .1$ mil layer of cholesteric liquid crystals were plotted. The "sandwich" was supported by three 10-mil tungsten wires over a heater in 10 ± 2 micron partial vacuum. From the plots it was estimated that the maximum temperature difference across the disks was $4.0 \pm .5^{\circ}\text{C.}$, and $3.0 \pm .5^{\circ}\text{C.}$ for separations between the heater and disk holder of $1.50 \pm .02$ in. and $.50 \pm .02$ in., respectively. The temperature in the central 50% of the disk area was constant to within about $.15^{\circ}\text{C.}$ These samples are expected to have a similar temperature distribution to those in the HV system.

B. COHESIVE PROPERTIES:

1. Pressure and Temperature Derivative of the Elastic Constants of SrF_2 - John Debesis, D. E. Schuele and C. Wong.

X The theoretical calculations of the elastic properties of SrF_2 using Axe's Shell Model have been completed by Dr. Chuen Wong, formerly of this laboratory and presently at Lowell Technological Institute. This analysis together with the experimental results which were reported in last years progress report are being incorporated into a technical report and it will be submitted for publication in the Journal of Physics and Chemistry of Solids. Briefly, the results on SrF_2 strengthen the work which was done of CaF_2 and BaF_2 by Dr. Wong while at Case Western Reserve University. This completes the study on this family of materials with the result that the basic shell model does predict the major contributions to their elastic properties.

2. The Elastic Constants of CdF_2 and Their Pressure Derivatives - G. Lanese, P. Prevey and D. Schuele.

In order to reduce the data from the dielectric measurements one needs to know the bulk modulus and its pressure derivative. Since this data was not available for CdF_2 measurements were undertaken by G. Lanese and P. Prevey, (Case Institute senior physics majors) as a project in our laboratory. The measurements have been completed with results listed below:

	Elastic Constant	Pressure Derivative
C_{11}	1.822×10^{12} dynes/cm ²	7.132
C_{12}	0.664	5.580
C_{44}	0.217	1.291
B_s	1.050	6.100

Even though this material has the same structure as CaF_2 , SrF_2 and BaF_2 , the data for CdF_2 does not fit into the analysis of Axe's Simple Shell Model. This is easily seen from a plot of the elastic constants and their pressure derivatives as a function of lattice spacing. The main difference between the electronic structure of Ca, Sr and Ba with Cd is that the filled shell below the s electrons is a p shell for the former and a d shell for the latter.

A technical report will be issued shortly and a paper submitted to the Journal of Physics and Chemistry of Solids.

3. Theory of Measurement of Third Order Elastic Constants - R. Hankey and D. Schuele.

A first draft of a paper on the theory of measurement of third order elastic constants is now complete. The work has not progressed as rapidly as we would like as the collaboration is now by mail since Dr. Hankey is now employed at Technitrol in Philadelphia. We hope to have the technical report completed shortly and submit the work for publication. Our results clarify many of the confusions and complications that now exist in the literature.

4. Temperature Derivatives of the Static Dielectric Constants of the Alkaline Earth Fluorides - C. Andeen, J. Fontanella and D. E. Schuele.

X Preliminary measurements have been made of the temperature variation of the static dielectric constants and losses of the alkaline earth fluorides. The high level of accuracy at which these measurements have been made have revealed some interesting results. In the region near 24°K, loss peaks were noted with a corresponding rise in the static dielectric constant. Above this temperature, the impurity dielectric constant appears to fall off as $1/T$. The shape of the loss peaks is Lorentzian. The results, then, reflect on the intrinsic dielectric constant, and closer investigation of these effects will be made.

5. Pressure Derivatives of the Elastic Constants of Semiconductors - D. Swyt and D. E. Schuele.

An attempt has been made to find an explanation of the discrepancy that exists between the low temperature Grüneisen parameter of the semiconductors Si and Ge determined from calorimetry and elasticity data. To this end, measurements have been made by a standard pulse echo technique of the elastic constant of Si, Ge, GaAs, InAs and InSb at 300, 195, 77 and 4.2°K. The pressure derivatives of the elastic constants have been measured by the same technique down to 77°K. A system for measuring the changes with pressure of the elastic constants by a standing wave resonance technique, employing frequency modulated RF, has been developed and measurements made using the system. While agreement between pulse echo and FM data at 77°K is reasonable for large pressure changes (to 30,000 psi), extreme irregulari-

ties and non-linearities in data on shear waves and for both longitudinal and shear waves for small pressure changes (to 2000 psi) indicate a high degree of unreliability for this kind of data. The number of measurements necessary for a good statistical determination of pressure derivatives at low temperature will not be undertaken. Final measurements will depend exclusively upon pulse echo data and pressure derivatives down to 77°K.

6. Elastic Properties of Lead in the Normal and Superconducting State - J. Debesis and D. E. Schuele.

A [110] zone refined lead crystal obtained from Material Research Corporation was used in this investigation. Initially, an attempt was made to repeat the work of Alers who measured the change in the elastic constants between the normal and superconducting states of lead. Alers used a lead crystal with a 0.2% Bi impurity. The reason the impurity was added was to reduce the ultrasonic attenuation in the normal state and to pin dislocations in the superconducting state which would normally give the velocity of sound an amplitude dependence. This amplitude dependence is thought to be produced by the strain amplitude of the sound wave unpinning the dislocations. In the normal state, these dislocations are strongly pinned from the interaction of the conduction electrons with the lattice; but, in the superconducting state, this interaction is absent and the dislocations are only weakly pinned. By lowering the transducer's driving voltage, it may be possible to reduce the strain amplitude of the sound wave to a point where it is of insufficient magnitude to unpin these dislocations.

Alers' experiment could not be repeated for lead for two reasons. First, the longitudinal velocity of sound in the superconducting state was strongly amplitude dependent. This was measured by first driving the sample normal by warming it then cooling it in zero magnetic field to 4.2°K in order to remove any trapped magnetic flux which could pin dislocations. The transducer's driving voltage was then varied from 500 to 20 mV. The measured change in the velocity of sound was linear in driving voltage and had a magnitude of approximately 200 ppm between the 500 and 20 mV limitations of the present equipment. These results were reproducible and as a further check the sample was driven normal with a 2 Kgauss magnetic field and the experiment repeated. There was no detectable change in the velocity of sound with driving voltage in the normal state. This amplitude dependence had the net effect of increasing the change in the velocity of sound between the normal and superconducting state as the driving voltage is increased. The linearity of this amplitude dependence indicated that with the present equipment the driving voltage could not be lowered to a point where the strain amplitude of the wave would have insufficient magnitude to unpin dislocations.

Magnetoacoustic oscillations in the ultrasonic attenuation at a frequency of 70 MHz indicated a $q\ell > 3$ where q is the wave vector and ℓ is the mean free path. Also weak magnetoacoustic oscillations in the velocity of a longitudinal sound wave were observed in the normal state at 10 MHz. These results indicate a relatively high purity lead crystal which bears on the amplitude dependence.

Since Alers observed changes in the sound velocity of less than 10 ppm for the lead alloy, these other effects completely overpower this change in pure lead. Consequently, the proposed experiment on the measurement of the changes in the elastic constants and their pressure derivatives between the normal and superconducting states in pure lead was abandoned. The experiment could have been performed with a lead alloy; but, alloying reduces the mean free paths of the normal state conduction electrons much faster than it pins dislocations in the superconducting state. As a consequence of this alloying, the normal state conduction electrons will not behave as those of the pure metal and any experimental results would be difficult to interpret.

Due to the recent publication of B. C. Deaton who repeated Alers experiment of the measurement of the change in the elastic constants between the normal and superconducting states of lead, some further investigation of lead appears necessary. Deaton used the same experimental technique employed in this laboratory's earlier investigation on lead and obtained results which were 30 times larger than Alers' results. Now, Deaton used a very high transducer driving voltage of 21 volts and observed no serious amplitude dependence of the velocity of sound. It is felt that with a driving voltage of this magnitude, the strain amplitude of the wave is great enough to have saturated this dislocation unpinning mechanism which gives rise to this amplitude dependence. From the earlier work by this laboratory on lead, this would lead to a very large erroneous result in the measured change.

To satisfactorily explain this discrepancy between Alers and Deaton's work, the lead crystals were given to Professor J. Trivisonno of John Carroll University who consented to collaborate with us and whose facilities will be used to ascertain the validity of Deaton's recent measurements.

7. Low-Temperature Pressure Derivatives of the Elastic Constants of Sodium - G. Lanese, P. Prevey and D. Schuele.

Measurements were attempted on the pressure derivative of the elastic constant C_{44} of sodium at 77°K. Extensive time was spent in attempting to make satisfactory acoustic bonds between the quartz transducer and the sodium crystal. We were unable to produce bonds which remained good to 77°K. In order to eliminate bond effects that could have explained the odd temperature dependence the Cornell group observed this care was quite necessary. With graduation, two of the above members left school and the attempt has been temporarily abandoned. We hope in the future to carry out these measurements with the aid of Dr. Trivisonno of John Carroll University who has much experience working with sodium.

8. The Elastic Constants and Their Pressure Derivatives of Cu-Ni Alloys - J. Debesis and D. E. Schuele.

During this past year, measurements were initiated and completed on the elastic constants and their pressure derivatives of Cu-Ni alloys at 300, 195 and 77°K with crystals of composition 0.0, 3.02, 6.02 and 9.73 atomic percent lead. The measurements were done using standard pulse echo techniques. A complete analysis of these measure-

ments as well as a review of the noble metal alloys is being undertaken.

9. The Pressure and Temperature Derivatives of the Static Dielectric Constants of LiF, NaF, NaCl, NaBr, KCl, and KBr - J. Fontanella, C. Andeen, and D. Schuele.

The experimental work on the room temperature (308°K) pressure derivatives of the static dielectric constants of LiF, NaF, NaCl, NaBr, KCl, and KBr is now complete. The results are:

	Units	LiF	NaF	NaCl	NaBr	KCl	KBr
$(\frac{\partial \epsilon_s}{\partial P})_T$	$10^{-12}(\frac{\text{cm}^2}{\text{dy}})$	-45.946	-27.377	-61.230	-81.261	-52.962	-60.866
$(\frac{\partial^2 \epsilon_s}{\partial P^2})_T$	$10^{-22}(\frac{\text{cm}^2}{\text{dy}})^2$	7.827	6.127	28.96	51.97	33.26	47.67
$(\frac{\partial^3 \epsilon_s}{\partial P^3})_T$	$10^{-33}(\frac{\text{cm}^2}{\text{dy}})^3$	-14.57	-13.36	-190.0	-547.4	-227.9	-534.2

The accuracies of the first, second, and third order pressure derivatives of the static dielectric constants are on the order of 0.2%, 2%, and 20% respectively except for the second and third order derivatives for LiF and NaF where the uncertainties are slightly higher due to the low absolute values of these quantities.

The determination of the temperature variation of the static dielectric constants of these crystals is still in the preliminary stages. Some results thus far for the 308°K temperature derivatives are:

	Units	LiF	NaF	NaCl	NaBr	KCl	KBr
$\left(\frac{\partial \epsilon_s}{\partial T}\right)_P$	$10^{-5}/^{\circ}\text{K}$	243.60	143.28	186.23	209.66	141.84	145.32
$\left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_P$	$10^{-7}/(^{\circ}\text{K})^2$	8.12	10.16	13.45	15.20	13.35	13.62

where the accuracies are about 0.5% and 25% for the first and second order derivatives respectively.

10. Accurate Determination of the Dielectric Constant by the Method of Substitution - C. Andeen, J. Fontanella and D. Schuele.

A new method for determining the dielectric constant of insulators has been developed. This technique improves the accuracy of the best previous measurements fifty fold. This work is reported in Technical Report No. 63 whose abstract follows:

A substitution method for highly accurate determination of the static dielectric constant of solids is presented along with techniques for refining capacitance measurements. The results for some alkaline earth fluorides are CaF_2 : 6.799, SrF_2 : 6.466, and BaF_2 : 7.359, and an alkali halide, KCl, is: 4.818.

11. The Low Frequency Dielectric Constants of LiF, NaF, NaCl, NaBr, KCl, and KBr by the Method of Substitution - John Fontanella, Carl Andeen, and Donald Schuele.

Very accurate measurements of the static dielectric constant of some selected alkali halides have been made and the results are described in Technical Report No. 66. The abstract follows:

The 1000 Hz 300°K dielectric constants of some alkali halides were measured to an accuracy of 0.01% by the method of substitution. Reproducibly different values for various crystals of the same type were obtained which varied beyond the experimental error. The ranges of results for various crystals of each type measured are: LiF, 9.0355-9.0360; NaF, 5.0719-5.0722; NaCl, 5.8940-5.8956; NaBr, 6.3957-6.3974; KCl, 4.8112-4.8182; and KBr, 4.8735-4.8762. The spread for each type of crystal is thought to be attributable to random trace impurities. The numbers are discussed in the light of past values.

12. The Low Frequency Dielectric Constants of the Alkaline Earth Fluorides by the Method of Substitution - Carl Andeen, John Fontanella, and Donald Schuele.

The most accurate measurements ever made on the static dielectric constant of the alkaline earth fluorides have been completed in our laboratory and the results are reported in Technical Report No. 67. The abstract follows:

The 1000 Hz 300°K dielectric constants of the alkaline earth fluorides were measured to an accuracy of 0.01% by the method of substitution. Reproducibly different values for various crystals of the same type were obtained which varied beyond the experimental error. The ranges of results for various crystals of each type measured along with further separation by manufacturer are: CaF_2 , Harshaw, 6.7984-6.4664, Optovac, 6.4700-6.4703; and BaF_2 , Harshaw, 7.3590-7.3595, Optovac, 7.3606-7.3630. The spread for each type of crystal is thought to be attributable to random trace impurities.

13. A Capacitive Gage for the Accurate Measurement of High Pressures - Carl Andeen, John Fontanella, and Donald Schuele.

The present primary standard used for the measurement of pressure is the dead weight gage. We have developed a secondary standard gage which uses the dielectric property of a single crystal as the sensor. This gage has many advantages over the dead weight gage and has an accuracy limited only by the primary standard. The initial calibration of this gage was carried out at the National Bureau of Standards using their primary standards. We expect this to be a major advance in the measurement of high pressures. A description of the gage and discussion is found in Technical Report No. 68, and is described in the following abstract:

A highly accurate and precise pressure gage which utilizes the 35°C, 2000 Hz dielectric constant of an ionic crystal, CaF_2 , is presented. The accuracy, stability, and convenience of such a gage are discussed comparing it to dead weight and manganin wire resistance gages. From a calibration at the National Bureau of Standards, the defining equation was found to be:

$$C/C_0 = 1 - AP + BP^2$$

where C_0 is the zero pressure capacitance, C is the capacitance at absolute pressure P , and the characteristic constants are:

$$A = 2.6063 \times 10^{-7}/(\text{psi})$$

and

$$B = 1.302 \times 10^{-13} / (\text{psi})^2.$$

14. Theory of the Measurement of the Continuous Wave Technique -

H. Deckman and D. Schuele.

This work is now complete and will be issued shortly as a technical report. The final computer work was done at Iowa State University by H. Deckman, who is now attending that university as a graduate fellow in the Department of Physics.

C. SOLID STATE THEORY

1. Properties of Disordered Systems - P. L. Taylor and S.-Y.

Wu.

The formal aspects of a calculation of the dynamics of disordered alloys and glasses have now been completed. A paper based on this work has been accepted for publication in the *Physical Review*, and has the following abstract:

A formalism is presented for the calculation of the spectrum of normal modes of a disordered solid by means of a perturbation theory that takes a mean-field model as its unperturbed system. A transformation is used that allows the long-range correlations in the low-frequency vibrational modes to be accurately taken into account. In the special case of a random substitutional alloy, a result is found which reduces to those of other workers when the limit of small mass difference of the constituents or low concentration is taken. Some aspects of the application of the theory to amorphous systems are also discussed.

2. Virtual Recoil Effects in Metals and Alloys - P. E. Nielsen and P. L. Taylor..

Our earlier ideas about the effect of virtual recoil on the thermopower of dilute alloys [*Phys. Rev. Letters* 21 893 (1968)] have now received gratifying confirmation in the experimental work of F. D. Manchester at the University of Toronto on alloys of hydrogen in palladium. A joint paper on this subject has been published [*Phys. Letters* 32A 161 (1970)] with the abstract:

The positive concentration-independent thermopower of PdH alloys at low temperatures is interpreted as strong evidence for the importance of virtual-recoil processes in leading to energy-dependent scattering of conduction electrons.

Work on the thermopowers of pure metals has also confirmed our preliminary calculation that the phenomenon normally called "phonon drag", and attributed to an imbalance in the phonon spectrum of metals may in fact be due to virtual recoil. An abbreviated report of this work has been published [Phys. Rev. Letters 25 371 (1970)] with an abstract that states:

The second-order effects of intrinsic two-phonon processes in the electron-phonon interaction are shown to give rise to a contribution to the thermopower of metals of a magnitude and shape identical to that previously attributed solely to phonon drag.

A more detailed account appears in Technical Report No. 65. The abstract of this report reads:

The electron-diffusion thermoelectric power (thermopower) of metals and dilute alloys is investigated over a wide range of temperatures in a simple model of free electrons with scattering characterized by a relaxation time τ . It is found that second-order corrections to the T-matrix for electron scattering involving intermediate virtual phonon states result in strongly energy-dependent corrections to τ , and thus greatly influence the thermopower. The primary results are first, that there exists a contribution to the electron-diffusion thermopower of a metal which has the same magnitude and general temperature-depen-

dence as that due to phonon drag, and second, that there is a term in the thermopower of an alloy which is strongly dependent upon the type of impurity present, and is important at low temperatures. The significance of these results in interpreting experimental data is discussed.

3. Electron-Ion Interactions in Glasses - J. Ferrante and P. L. Taylor.

Preliminary calculations have suggested that ion-recoil effects in switching phenomena in amorphous materials may only be important in a rather limited range of circumstances. Our theoretical analysis of this problem is accordingly proceeding at a more gentle rate to allow more experimental evidence to appear in the literature. An alternative study has also been pursued of the nature of electron states in disordered materials by a computation of the electron density of states in some one-dimensional systems. A new method of performing this calculation is already yielding some interesting information on the nature of electron states at band edges. X

4. Bloch Electrons in Magnetic Fields - P. L. Taylor and H. H. Hosack.

Our calculation of the Helmholtz energy of a simple system of Bloch electrons in a uniform magnetic field is now almost completed, and will be submitted for publication shortly. We have also pursued the transfer-matrix approach and have shown that the energy-level structure can be expressed in terms of the roots of a remarkably simple equation of the form

$$\sin \alpha \epsilon = p \sin \beta \epsilon$$

The parameter p varies from 0 to 1, and describes the strength of the lattice potential. When $p = 0$ the solutions $\epsilon = n\pi/\alpha$ describe the equally-spaced Landau levels of a free electron in a magnetic field, while when $p = 1$ the alternative solutions $\epsilon = (2n + 1)\pi/(\alpha + \beta)$ and $\epsilon = 2n\pi/(\alpha - \beta)$ represent the periodic open orbits and so-called "lens" orbits respectively. This work is also being prepared for publication.

5. The Knight Shift - J. Gubernatis and P. L. Taylor.

Work has continued on the problem of the electron amplitudes in metals in magnetic fields in two principal directions. Some progress has been made in the generalization of a modified Fermi-Segré formula to predict the Knight shift in realistic models, although the hoped-for connection of this quantity with the optical properties has not yet been achieved.

On another front the response of the electron wave functions themselves to a weak but spatially varying magnetic field has been analyzed and found to confirm some commonly-held beliefs concerning the diamagnetism of insulators.

6. Theory of Magnetoresistance and Size Effects in Metals - G. E. Juras and P. L. Taylor.

The research described in Technical Report No. 61 has been extended by the completion of some numerical computations of the galvanomagnetic tensor of a simple anisotropic model. This work has been

accepted for publication in the Physical Review. A more specialized point concerning the interpretation of experimental results for the low-field galvanomagnetic effects has been published [Physics Letters, 32A 452 (1970)], and carries an abstract that states:

Analysis of the conductivity of metals at low magnetic fields yields a sufficient condition that the high-field magnetoresistance should saturate.

A large part of the proposed calculations on the radio-frequency size effect in metals have now been completed. The results of these investigations have been presented in the two articles.

"Angular Dependence of Surface Scattering" by G. E. Juras, published in the Physical Review Letters, 24 390 (1970) and "Influence of Surface Scattering on the Radio-frequency Size Effect" by G. E. Juras to be published in the Physical Review, October 15, 1970. The abstracts are, respectively:

Calculations of the rf surface impedance of a thin metal plate as a function of a dc magnetic field applied parallel to the faces of the plate reveal that one can measure experimentally the critical angle of collision with the surface, if such an angle exists, below (above) which electron surface scattering is mostly specular (diffuse).

The surface impedance of a thin metal plate excited by a rf electromagnetic field is calculated as a function of external dc magnetic field applied in the plane of the plate under the nonlocal conditions of the anomalous skin effect. A linearized Boltzmann equation in the relaxation time approximation for isotropic bulk scattering is solved

by means of a generalized kinetic formulation which (i) describes the surface scattering by means of a specularity function that can depend on the angle of collision of the electron trajectories with the surface and which (ii) contains an ineffectiveness parameter in the non-local form of Ohm's law, thus providing a measure for the possibility that electrons colliding with the boundaries are less effective than bulk electrons in linking the current density at one point of the conductor with the electric field at another point. This generalized path-integral solution of the Boltzmann equation is coupled with Maxwell's equations, and the resulting integro-differential equation is solved for the spatial distribution of the electric field inside the metal plate using the numerical procedure discussed in an earlier publication by the author. This is done for both the symmetric and antisymmetric modes of excitation of the plate by the rf field in the case of a model cylindrical Fermi surface. The resulting curves for the surface impedance versus the applied dc magnetic field exhibit characteristic features which are greatly influenced by the explicit choice of the specularity function and/or the ineffectiveness parameter. It is suggested that these features can be used in conjunction with experiment to determine the correct parameters for the surface scattering mechanism.

Size effects in the magnetoresistance coefficients, including the Hall effect, are currently being studied. Additional problems related to the radiofrequency size effect (line shapes in tilted magnetic fields, transmission line shapes, etc.) are also under investigation.

APPENDIX I

Personnel Associated with the Contract

Professional Staff

Richard W. Hoffman, Professor of Physics
Donald E. Schuele, Associate Professor of Physics
Philip L. Taylor, Associate Professor of Physics
George E. Juras, Research Associate

Research Assistants and Thesis Students

C. G. Andeen
R. E. Chase
J. R. Debesis
F. A. Doljack
J. Ferrante
J. J. Fontanella
J. J. Gubernatis
M. Kwan
P. E. Nielsen
R. E. Rottmayer
R. W. Springer
D. A. Swyt
M. N. Varma
A. C. Zuppero

Summer Graduate Students

M. Alexander
C. Hagerling
J. Petterson

Undergraduate Students

H. Deckman
A. Lanese
P. Prevey
J. Strok

Machinist

J. Jaroscak

Secretaries

Z. M. Clifford
A. Munoz
M. E. Young

Appendix II

Technical Reports

No. 62	Mössbauer Effect of Ultra-thin Iron Films	A. C. Zuppero	COO-623-149
No. 63	Accurate Determination of the Dielectric Constant by the Method of Substitution	C. Andeen, J. Fontanella and D. Schuele	COO-623-150
No. 64	Structure and Intrinsic Stress of Platinum Thin Films	R. E. Rottmayer	COO-623-151
No. 65	Theory of Thermoelectric Power in Metals and Alloys	P. E. Nielsen and P. L. Taylor	COO-623-152
No. 66	The Low Frequency Dielectric Constants of LiF, NaF, NaCl, NaBr, KCl, and KBr by the Method of Substitution	Carl Andeen, John Fontanella, and Donald Schuele	COO-623-153
No. 67	The Low Frequency Dielectric Constants of the Alkaline Earth Fluorides by the Method of Substitution	Carl Andeen, John Fontanella, and Donald Schuele	COO-623-154
No. 68	A Capacitive Gage for the Accurate Measurement of High Pressures	Carl Andeen, John Fontanella, and Donald Schuele	COO-623-155

Appendix III

Publications

The following papers were cited in previous years' reports.

Reprints are now being sent under separate cover.

Ultrasonic Parameters in the Equation of State of the
Sodium and Potassium Halides, R. W. Roberts and C. S.
Smith, J. Phys. Chem. Solids 31, 619 (1970) COO-623-131

Saturation Magnetization and Perpendicular Anisotropy of
Nickel Films, R. Baron and R. W. Hoffman, Jour. Appl. Phys.
41, 1623 (1970) COO-623-132

Third Order Elastic Constants of Al_2O_3 , R. E. Hankey and
D. E. Schuele, J. Acoust. Soc. Amer. 48, 190 (1970)
COO-623-140

Low Temperature Grüneisen Parameter of RbI from Elasticity
Data, J. J. Fontanella and D. E. Schuele, J. Phys. Chem.
Solids 31, 647 (1970) COO-623-141

Lorenz Numbers of Dilute Ag Alloys, D. Jha, M. H. Jericho
and P. L. Taylor, Phys. Rev. B 1 1980 (1970) COO-623-144

Mössbauer Spectra of Thin Iron Films, A. C. Zuppero and
R. W. Hoffman, J. Vac. Sci. Tech. 7, 118 (1970) COO-623-145

Boundary Conditions for Stress Measurement Using a Cantilevered Beam, R. E. Rottmayer and R. W. Hoffman, J. Vac. Sci. Tech. 7, 461 (1970) COO-623-146

Thin Films in Electronics, R. W. Hoffman, Trans. N.Y. Academy of Science, II, 31, 868 ⁽¹⁹⁶⁹⁾~~(1970)~~ COO-623-147

The following papers have been published or submitted for publication but no reprints are available as yet.

Pressure and Temperature Derivatives of the Elastic Constants of AgCl and AgBr, K. F. Loje and D. E. Schuele, J. Phys. Chem. Solids 31, 2051 (1970) COO-623-138

Angular Dependence of Surface Scattering, G. E. Juras Phys. Rev. Letters, 24, 390 (1970) COO-623-157

Evidence of Virtual Recoil in the Thermopower of PdH Alloys, F. D. Manchester, P. E. Nielsen and P. L. Taylor, Phys. Letters, 32A, 161 (1970) COO-623-158

A New Effect in the Electron-Diffusion Thermopower of Pure Metals, P. E. Nielsen and P. L. Taylor, Phys. Rev. Letters 25, 371 (1970) COO-623-159

Interpretation of Low-Field Galvanomagnetic Effects, P. L. Taylor, Phys. Letters 32A, 452 (1970) COO-623-160

Dynamics of Disordered Alloys and Glasses, P. L. Taylor and Shi-Yu Wu, Phys. Rev. B, 15 Sept. COO-623-161

Influence of Surface Scattering on the Radio Frequency Size Effect, G. E. Juras, Phys. Rev. In Press, publication date, 15 October 1970 COO-623-162

Accurate Determination of the Dielectric Constant by the Method of Substitution, Carl Andeen, John Fontanella and Donald Schuele, Rev. of Sci, Inst. In Press, publication date Nov. 1970. COO-623-150

Low Frequency Dielectric Constants of LiF, NaF, NaCl, NaBr, KCl and KBr by the Method of Substitution, Carl Andeen, John Fontanella and Donald Schuele, Phys. Rev. In Press, publication date Dec. 1970 COO-623-153

Theory of Galvanomagnetic Effects in Metals, Gale Fair and P. L. Taylor, Accepted by Phys. Rev. COO-623-163

Structure and Intrinsic Stress of Platinum Films, R. E. Rottmayer, and R. W. Hoffman, Accepted by J. Vac. Sci. Tech. COO-623-151

The Low Frequency Dielectric Constant of the Alkaline Earth Fluorides by the Method of Substitution, Carl Andeen John Fontanella and Donald Schuele, Submitted to J. App. Phys. COO-623-154

A Capacitive Gage for the Accurate Measurement of High
Pressures, Carl Andeen, John Fontanells and Donald Schuele,
Submitted to Rev. Sci, Inst. COO-623-155

UHV Mössbauer Emission Spectra of Thin Iron Films, M. N.
Varma and R. W. Hoffman, Submitted to J. Appl. Phys.
COO-623-164

Appendix IV

EQUIPMENT REPORT

AEC Contract AT(11-1)-623

Case Western Reserve University

for the period 1 February 1970 through 30 September 1970

PURCHASED TO DATE: (30 September, 1970)

<u>ITEM</u>	<u>DATE PURCHASED</u>	<u>COST</u>
-------------	-----------------------	-------------

None

October 1970