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Abstract

The QUEGS facility at MURR and the cryogenic scattering facility at Purdue University have produced a number of new results and demonstrated the range of potential applications of high resolution, high intensity Mössbauer scattering. This work has been carried out by both MU and Purdue researchers and includes published results on Na, W, pentadecane, polydimethylsiloxane and other systems, with publications in preparation on alkali halides, glycerol, and NiAl. Recently new collaborations have been initiated which will substantially enhance our efforts. These are with W. Steiner (Vienna), G. Coddens (Saclay), and R.D. Taylor (Los Alamos). Steiner is experienced with ^{57}Fe Mössbauer scattering while Coddens specializes in quasielastic neutron scattering; both of these areas naturally complement our work. R.D. Taylor has pioneered Mössbauer spectroscopy from the time of its discovery and has already made important contributions to our study of lattice dynamics and superconductivity for lead alloyed with small quantities of tin. At the same time a significant instrument upgrade is underway, funded in part by the DOE-URIP program.

The QUEGS facility will be used for a variety of studies in condensed matter science, concentrating on diffusion in solids (C_{60}, Pb salts, and quasicrystals) and liquids (such as glycerol), phase transitions (especially in lithium heptagermanate), and Debye-Waller studies including the role of doped W in altering T_c and J_c for W doped 123 superconductors. The availability of a multi-beam facility will enable us to optimize each beam line for a specific class of problem, especially distinguishing those which use high intensity and poor q resolution from those for which better q resolution is required. We expect to develop further the collaborations with Steiner and Coddens in order to have complementary data on systems we will study with the QUEGS instrument. Further development of the MICE technique, using either an oscillating source or an oscillating monochromating crystal, will also help to enhance signal-to-noise ratios in important cases. The interference and line-shape studies have been very fruitful, resulting in many publications and the most accurate interference parameters to date. While we will use the knowledge gained from these studies in applying our technique to materials problems, they will not be pursued as an independent research line in the present renewal proposal.

Contents

I. Introduction

The University of Missouri Research Reactor (MURR) provides a unique resource for the production and utilization of high activity radioactive sources. The central flux (6×10^{14} $\frac{n}{cm^2 \cdot sec}$) and 1 week cycle especially benefit programs using double neutron capture and short half-life isotopes. The quasielastic gamma-ray scattering (QUEGS) instrument and the complementary laboratory at Purdue University have been developed with DOE support to use high activity Mössbauer sources for scattering and Mössbauer research on materials. QUEGS uses 100 Ci ^{183}W sources produced by irradiation of 100% abundant ^{181}Ta. With its 5.1 day half-life it is a practical source of 46.5-keV Mössbauer photons for scattering only if it can be replaced on a rapid (1 week) basis as is done at MURR. The sources are cooled to 80K and a single beam is extracted from a shielding cask. A variety of different configurations for direct beam and filtered beam geometries as well as different detection methods are employed. The Purdue facility uses a few longer-lived, but unconventional sources such as ^{170}Tm, and allows for source cooling to liquid He temperature, giving a significant enhancement in recoil-free fraction for many resonances. After use the sources are returned to MURR for re-irradiation.

During the last 4 year funding period significant progress has been made with these facilities, which have addressed specific problems in liquids and solids (Sec. II) but which have also exposed deficiencies in the initial construction that have limited their utility due to either a lack of intensity or to time conflicts on a single beam instrument. Fortunately we have been awarded a DOE-URIP grant to upgrade and modify the QUEGS facility in order to provide multiple beam lines, each of which will be optimized for a different type of measurement. A wider variety of sources will also be afforded by cooling them to 20K. This upgrade (Sec. III), which is underway, will provide dedicated beams for liquid scattering, single crystal studies, and studies of lattice dynamics and hyperfine measurements on a wide variety of condensed matter, while providing an additional beam for technique development and methodology. With these improvements in place we will be able to undertake a far more comprehensive research program in the areas of Debye-Waller effects such as crystal anharmonicity, diffusive motions in liquids and solids, and lineshape studies especially related to resonant scattering processes and lattice dynamics (Sec. IV).

II. Progress Report

A. General Review of Progress During Last 4 Year Support Period

1. Current students working on project

Purdue University	Source of Support	Grade Index (6.0 maximum)
John Day (U.S.)	DOE - Purdue	5.51
Scott Dickson (U.S.)	DOE - Purdue	5.26
Mi-Ae Park (Korea)	Fellowship	5.93
Carmen Shepard (U.S.)	Teaching	5.88
Ralph Wagoner (U.S.)	DOE - UMC	5.55
Ji Zhang (China)	Teaching	5.80
University of Missouri - Columbia		
Ken Barnes	DOE - UMC	5.00

- Wagoner is expected to complete his Ph.D. in August 1992. He received the Lark-Horowitz prize given once per year at Purdue for the outstanding thesis research by a graduate student at Purdue University.
- All Purdue students have completed their course work and are pursuing thesis research full time. Ken Barnes (UMC) is a masters student who is expected to complete his degree in the coming academic year.

2. Honors and special achievements by principal investigators received in last 4 year support period.

J. Mullen:

- Named a member of the seven man Organizing Committee for the International Conference on Applications of the Mössbauer Effect 1993 (ICAME '93). This conference is expected to bring together over 600 of the leading Mössbauer spectroscopists from around the world, and is featuring such well recognized physicists as Rudolph Mössbauer and Hans Franenfelder.
- The Program Chairman for ICAME '93, a committee comprised of 24 recognized scientists from every part of the world.

Guy Schupp:

- Was promoted to Full Professor in recognition of his work, which has been supported by D.O.E.

William Yelon

- Publication Co-Chairman, Magnetism and Magnetic Materials Conference (MMM) 1989 - 1991; InterMag '92 Editor.
- Oak Ridge Associated Universities (ORAU) Visiting Scholar, 1990 - 91.

3. Ph.D. Theses Resulting From The D.O.E. Sponsored Research.

- Bruce Bullard, "Mössbauer Studies in Tungsten, Iridium, and Terbium Using Line-Shape Analysis." Purdue University, December 1990.
- Ammar Djedid, "Precise Lineshape Measurements Using an Analytic Mössbauer Function." Purdue University, May 1988.
- Lowell Crow, "Mössbauer γ-ray Scattering in Silicon and Sodium." University of Missouri, December 1987.

4. List of Publications covering D.O.E. Grant Period 1988-1992.

1. J.G. Mullen, A. Djedid, D. Cowan, G. Schupp, M.L. Crow, Y. Cao, and W.B. Yelon, Physics Letters **A127**, 242 (1988). "Representation of Lineshape Parameters and Deconvolution of Mössbauer Spectra."

2. J.G. Mullen, A. Djedid, B. Bullard, G. Schupp, D. Cowan, Y. Cao, M.L. Crow, and W. Yelon, Hyperfine Interactions **40**, 123 (1988). "Precise Determination of Mössbauer Lineshape Parameters Including Interference."

3. J.G. Mullen, A. Djedid, G. Schupp, D. Cowan, Y. Cao, M.L. Crow, and W.B. Yelon, Physical Review **B37**, 3226 (1988). "Fourier-Transform Method for Accurate Analysis of Mössbauer Spectra."

4. G. Haley, J.G. Mullen, and J.M. Honig, Solid State Communications, **69**, 285 (1989). "First Order Change in Hyperfine Interaction at the Verwey Transition in Magnetite."

5. M.L. Crow, G. Schupp, W.B. Yelon, J.G. Mullen, and A. Djedid, Physical Review **B39**, 909 (1989). "Temperature Dependence and Anharmonicity of the Debye-Waller Factor in Sodium Metal Using Mössbauer Gamma-ray Diffraction."

6. B.R. Bullard, J.G. Mullen, and G. Schupp, Hyperfine Interactions **55**, 1127 (1990). "Using Lineshape to Precisely Determine Recoil-free Fraction: Application to Tungsten. "

7. R. Wagoner, B. Bullard, M. May, S. Dickson, and J.G. Mullen, Hyperfine Interactions **58**, 2687 (1990). "Time Dependence of the Source Recoilless Fraction for a Cobalt-57 in Rhodium Source."

8. S.R. Hong, G. Haley, and J.G. Mullen, Hyperfine Interactions **57**, 2221 (1990). "Iron Mössbauer Spectra of Lava from Jeju Island and its Similarities to Moon Basalts."

9. B.R. Bullard and J.G. Mullen, Nucl. Instr. and Meth. **B51**, 198 (1990).

10. G. Schupp, B. Hammouda, and C.M. Hsueh, Phys. Rev. **A41**, 5610 (1990).

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12. J.G. Mullen, B.R. Bullard, and G. Schupp, Proceedings of the Zakopane School of Physics, accepted for publication as a part of the proceedings, World

Scientific Publishing.

13. B.R. Bullard, J.G. Mullen, and G. Schupp, Submitted for publication in the Physical Review, "Mössbauer Line-Shape Parameter for ^{183}W and ^{191}Ir in Metallic Tungsten and Iridium.
14. B.R. Bullard and J.G. Mullen, Submitted for publication in the Physical Review, " Mössbauer Line-Shape Parameters for ^{159}Tb in $TbAl_2$ and Tb_4O_7.
15. R.A. Wagoner, B.R. Bullard, J.G. Mullen and G. Schupp, accepted for publication, Hyperfine Interactions, "Precision Measurements of Recoil-free Fraction and Interference with Hundred Curie Sources."
16. R.A. Wagoner, J.G. Mullen and G. Schupp, accepted for publication, Physics Letters B, "Double Absorber Mössbauer Spectroscopy in ^{183}W."
17. M. Park, P.A. Polstra and J.G. Mullen, Submitted to American Journal of Physics for publication, "Analytic Representations of the Mössbauer Recoilless Fraction, Debye-Waller Factors, Lattice Energies, and Heat Capacities."
18. G. Schupp, W.B. Yelon, R. Law, manuscript in preparation to be submitted to Solid State Communications, "Mössbauer Scattering Experiments on the Nature of Martensitic Phase Transition $Ni_{0.63}Al_{0.37}$."

5. Invited Talks J. G. Mullen (1987 - Present).

1. Unique Signatures in Mössbauer Spectroscopy and Deconvolution of Spectra, Jet Propulsion Lab, June 10, 1987.
2. Mössbauer Diffraction Experiments at the Research Reactor Facility, University of Missouri at Rolla, Chemistry Department, May 2, 1987.
3. Lineshape Determination in Mössbauer Spectroscopy, The University of Missouri Research Reactor Facility, June 6, 1987.
4. Precision Determination of Mössbauer Line-shape Parameters Including Quantum Interference, The University of Auckland, New Zealand, August 11, 1987.
5. Precise Determination of Mössbauer Lineshape Parameters Including Interference, ICAME '87, Melbourne, Australia, August 16-21, 1987.

6. True Mössbauer Line Shape and the Determination of Quantum Interference, Purdue University, September 3, 1987.
7. Gamma Ray Scattering, The University of Missouri University Research Reactor Facility, September 29, 1987.
8. Precision Determination of Mössbauer Lineshape and Quantum Interference, Johns Hopkins University, March 2, 1988.
9. Testing Nuclear Dispersion Theory, University of Missouri at Columbia, March 7, 1988.
10. Fourier-transform Mössbauer Spectroscopy: A New Tool for The study of Fundamental Physics, University of Texas at El Paso, May 26, 1988.
11. Using the Fourier-Transform Method of ME Spectroscopy for Precision Determination of the Recoilless Fraction, Zakopane School of Physics, Zakopane, Poland, May 2, 1990.
12. Measuring Recoilless Fractions and Interference Parameters Using Super-Intense Sources of Tungsten - 183, Johannes - Gutenberg University, Maine, F.R.G., May 8, 1990.
13. Probing Fundamental Physics with the Mössbauer Effect, Purdue University, August 27, 1990.
14. Mössbauer Effect with Hundred Curie Sources, University of Alabama, Tuscaloosa, AL, March 4, 1991.
15. Precision Measurements of Recoil-free Fraction and Interference with Hundred Curie Sources, Stanford, CA, March 15, 1991.
16. Basic Physics and the Mössbauer Effect, Purdue University, September 1991.

6. Invited Talks G. Schupp (1987 - Present).

1. Scattering Studies with High Intensity Mössbauer Sources at MURR, Hahn-Meitner Institute, W. Berlin, Germany, May 30, 1988.
2. Topics in Mössbauer Scattering, Kansas State University, January 30, 1991.
3. Mössbauer Diffraction with High-Intensity Sources, Kansas State University, January 31, 1991.

4. Mössbauer Scattering Studies with High-Intensity Sources, Colorado State University, February 4, 1991.
5. Mössbauer Scattering Studies with High-Intensity Sources, Tennessee Technical University, September 24, 1991.
6. Mössbauer Scattering Studies with High-Intensity Sources, University of Idaho, March 30, 1992.
7. Mössbauer Scattering Studies with High-Intensity Sources, Boise State University, April 3, 1992.
8. Mössbauer Scattering Studies with High-Intensity Sources, Idaho State University, April 6, 1992.
9. Mössbauer Scattering Studies with High-Intensity Sources, Utah State University, April 8, 1992.

B. Quasielastic Scattering Studies on Glycerol.

Progress has been made in better understanding the quasielastic scattering data already collected on glycerol and in planning further experiments. Figure 1 shows a plot of the fractional broadening, $\Delta\epsilon/\Gamma$, versus T/η, where T is the absolute temperature and η is the viscosity. As discussed by Singh and Mullen [1], the early prediction by Singwi and Sjölander [2], that diffusive motions could be studied by measuring the broadening of the Mössbauer lineshape, can be combined with the Einstein-Stokes relation in the continuous diffusion limit to give

$$\frac{\Delta\epsilon}{\Gamma} = \frac{4\pi\tau k}{3\lambda^2 R}\,\frac{T}{\eta},$$

where $\Delta\epsilon$ is the incremental broadening of the Mössbauer resonance of width Γ, τ is the mean nuclear lifetime, k is Boltzmann's constant, λ is the wavelength of the Mössbauer gamma rays and R is the radius of the diffusing entity. The data are well represented by a straight line and hence agree with the above equation, but the radius R determined form the slope is 122 Å. This value is much larger thant the "d" spacing for glycerol ($C_3H_5(OH)_3$) of 4.6 Å (determined from the position of its liquid structure peak at q = 1.36 $Å^{-1}$), which is consistent with intuitive estimates for the intermolecular spacing.

The fact that experimentally the width broadens approximately as T^2 above the freezing point as reported in our progress report last year (see the inset in Fig. 1), rather than $T^{1/2}$ as expected for a simple coherent scatterer, was what first led us to propose that hydrogen bonding was playing a major role in the scattering process. Viewed in terms of a molecule self diffusing in a viscous liquid, however, we find the expected T/η dependence but with an effective radius some 25 times larger than expected. Understanding the large value for diffusing radius and how it is possibly related to hydrogen bonding needs further study. When time is available on QUEGS, the scattering function, $S(\vec{q},\omega)$, needs to be measured at q-values away from the liquid structure peak at different temperatures. For example the broadening (or lack of it) at high temperature at $q = 0$ would be particularly interesting. To do this experimentally, however, will require using the filtering crystal before the sample, otherwise the $q = 0$ direct beam will overload the detector. This change will require longer counting times and is precisely the type of study which will be accommodated by the QUEGS upgrade (see Sec. III, B).

Shown as an inset in Fig. 1 is the broadening versus temperature curve presented last year. A better mathematical representation for the experimental lineshape obtained with our rotor (absorber) for highly broadened photons (100 μeV) has been recently worked out [3] and used to re-analyze these data. While not affecting the overall trend of the plots in Fig. 1, the magnitude of the broadening from the latest analyses seems to be significantly larger than earlier, but further tests of this new fitting procedure need to be made. Greater broadening, of course, gives smaller values for R discussed above.

The Department of Physics at MU has recently hired Paul Miceli, Bellcore, Red Bank, N.J. who will come 9/92 to set up his programs in x-ray and neutron scattering. Miceli has also indicated an interest in our Mössbauer scattering apparatus (technique) and it is anticipated that his knowledge of the field will significantly help our research efforts in this area.

ΔE/Γ
T/η (K/poise)
0
500
1000
2000
3000
4000
5000
6000
1
2
3
4
5
6
7
8
ΔE (μev)
T°C
0
20
40
60
80
100
120
10
20
30
40
50
60

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2. Singwi, K.S. and A. Sjölander, Phys. Rev. 120, 1093(1960).
3. Wagoner, R.A., private communication.

C. Gamma-ray scattering from alkali halides

We have succesfully completed an x-ray diffraction type experiment using 46.5-keV gamma rays and Mössbauer analyzers. The small energy width of the Mössbauer analyzers (2.5 μeV) allows energy resolution not available in x-ray or even neutron scattering methods. This increased energy resolution means that the probing radiation can be considered effectively monochromatic, removing the energy dependence of the inelastic component to scattering. The result is that thermal diffuse scattering, a major plague to x-ray workers, can be approximated as a simple "flat" background. This technique is particularly suited to analysis of dense crystals, such as tungsten and lead, where the attenuation of x rays is often prohibitive.

A beam of 46.5-keV gamma rays from ^{183}Ta was Bragg scattered at room temperature from an alkali halide crystal in transmission geometry. We Doppler shifted a natural tungsten foil (analyzer) first in a position between the tantalum source and the crystal (before position), and then in a position between the crystal and the photon detector (after position).

The small energy width of the resonance photons means that any phonon interaction (inelastic scattering) will result in the scattered resonant photon's energy being shifted sufficiently to cause it to appear as a 46.5-keV nonresonant photon. This reduces the observed effective source recoil-free fraction in the after position as compared to the before position. This energy width is also small enough that the probability of an incident nonresonant photon being inelastically scattered to the resonance energy is negligible.

The Mössbauer lineshape in the before case is that of the standard Mössbauer transmission experiment, and the count number C is given by:

$$C(x) = C_o \left\{ 1 - f_{sb} + \frac{2f_{sb}}{\pi} \int dx' \frac{e^{-i\mathcal{L}(2x')}}{1 + 4(x' - x)^2} \right\} \qquad (1)$$

where

$$\mathcal{L}(2x') = \frac{(1 - 4\beta x')}{1 + 4x'^2}$$

and we have made use of the dimensionless variables $x = (E_o v/c - E_r)/\Gamma$ and $x' = (E - E_o)/\Gamma$. The Doppler velocity of the analyzer is v, E_r is the difference in transition energy between the ^{183}Ta source nuclei and the ^{183}W absorber nuclei in the analyzer, $E_o = 46.5$ keV is the resonance energy, β is the interference parameter, and the energy level width is given by Γ. Finally, f_{sb} is the measured fraction of the 46.5-keV photons incident on the absorber, which in the before case is the same as the resonance fraction of the source beam itself, i.e. $f_{sb} = f_{so}$, and C_o is the count accumulation per channel off resonance.

The lineshape for the after position is of the same form, only now f_{sb} must be replaced by f_{sa}, the resonant fraction incident on the absorber in the after position, given by

$$f_{sa} = \left(\frac{\epsilon}{\epsilon + i} \right) f_{so},$$

where ϵ and i are defined as follows. If the number of 46.5-keV photons incident on the crystal is N, the number scattered into the detector elastically is given by ϵ N, and the number inelastically scattered, with energy still within the discriminated energy window centered about 46.5-keV, is given by i N. The small difference in energy between resonant and nonresonant, which is beyond the resolution of our germanium detector, means that these definitions for ϵ and i apply to both types of 46.5-keV gamma rays. From the above equations we have,

$$F = \frac{f_{sa}}{f_{sb}} = \frac{\epsilon}{\epsilon + i}. \qquad (2)$$

By least squares fitting to the before and after case, we arrive at values for f_{sb} and f_{sa}, and hence of F. Our measured values of F are given in the following table of F for various Bragg reflections. We find a remarkably large fraction of the scattered

radiation remains recoilless (>94%), even for the (600) reflection of NaCl. This is particularly noteworthy in that the integrated elastic intensity of the (600) reflection is a full order of magnitude smaller than the (200) reflection for NaCl. A value of F = 100.0 (3)% for the (200) reflection of LiF shows that these crystals are excellent gamma-ray monochromators, and they are excellent for calibrating before-after experiments where direct beam counting leads to difficult background corrections and prohibitive count rates.

Values of $F = f_a/f_b$.

	reflection	F (measured)	F (calculated)
NaCl	(200)	0.980(4)	0.984
	(400)	0.966(4)	0.964
	(600)	0.949(6)	0.949
NaF	(200)	0.962(3)	0.973
	(400)	0.947(3)	0.945
	(600)	0.942(5)	0.939
LiF	(200)	1.000(3)	0.996
	(400)	0.991(3)	0.993

We have also derived expressions for ϵ and i using the Debye model. Using these expressions we performed a two parameter fit to F which gave a value of 276(93) K for the Debye temperature of NaCl, in good agreement with heat capacity measurements. Because of the large errors in θ_D determined this way we fitted the data with specific heat values of the Debye temperature and in terms of this one parameter fit involving

the coefficients of i/e we obtained the values shown in the last column of the table displaying $F = f_a/f_b$. The agreement between measured values of F and those calculated with a one parameter fit are excellent.

Our results on the (200) reflection of LiF are in good agreement with the results of Mullen and Stevens [1], but were greater than the values of O'Connor and Butt [2]. These earlier experiments were done with ^{57}Co and had much lower intensity and correspondingly poorer collimation.

Our data reported here was taken in about two weeks of counting, and this is a great improvement in poorly collimated ^{57}Fe experiments which require months or years for much lower accuracy.

References

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2. D.A. O'Connor and N.M. Butt, Phys. Letters **7**, 233 (1963).

D. Lattice Dynamics in Metals

1. Sodium Metal

The Debye-Waller factor of sodium has been measured [1] as a function of temperature from 80 to 295 K using Mössbauer gamma-ray scattering. The high energy resolution provided by this technique allowed experimental separation of the elastic scattering from the inelastic thermal diffuse scattering. The results were compared with the harmonic model using intergrations over dispersion curves from the neutron-scattering measurements of Woods et al. [2] and the lattice-dynamics calculations of Glyde and Taylor [3]. The Debye-Waller exponent was shown to exceed the harmonic prediction by 23% at room temperature, and this difference is attributed to anharmonic terms in the interatomic potential. Our results and

the molecular dynamics calculations of Shukla and Heiser [4] agree to within 5% at the highest temperature studied.

In a more recent study by Shukla and Taylor [5], a comparison was made between our Mössbauer (and earlier x-ray) results and calculations based on three different theoretical methods. To quote their abstract

> "Excellent agreement is found between the results of these three methods and the Mössbauer experimental results. The x-ray results are also in very good agreement with the Mössbauer data where the temperatures overlap in the measurements."

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3. H.R. Glyde and R. Taylor, Phys. Rev. **B5**, 1206 (1972).
4. R.C. Shukla and G.A. Heiser, Phys. Rev. **B33**, 2152 (1986).
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2. Tungsten Metal

Tungsten metal is one of the densest metals of all of the elements and has the highest melting temperature. We have measured the recoilless fraction for tungsten from 80 to 1067 K, using direct fitting of the Mössbauer data to the convolution integral. The results are summarized in a recent paper [1] and these show that anharmonic effects are already being seen as low as 700 K.

Except for the very highest temperature datum point, we were able to account for our results extremely well by only including a cubic term in the potential, by means of a Gruneisen constant correction.

This data is unique and to the best of our knowledge it has not been possible to obtain such high accuracy f(T) measurements ever before. The small role of

Debye-Waller factors compared to heat capacity measurements in the development of lattice dynamics has mainly been due to this limited accuracy to Debye-Waller measurements. The direct demonstration that it is now possible to measure Debye-Waller factors and recoilless fractions to accuracies of order 1% or better, means that these numbers will be much more useful in the evaluation of lattice dynamic calculations. Both of these measured quantities can be expressed as Debye type integrals, but with differing weighting factors within the integrals.

We are currently cooperating with Professor Shukla, Brock University, in attempting a more detailed understanding of anharmonic effects in tungsten, and our future plans in this area will be given in Sec. IV, D.

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1. B.R. Bullard, J. G. Mullen, and G. Schupp, Phys. Rev. B43, 7504 (1991).

3. Tin-Doped Lead

This research was motivated by a striking deviation from expected physical behavior reported by Shechter, Stern, Yacoby, Brener, and Zhang (SSYBZ) in a Physical Review Letter dated 25 September 1989 [1]. Specifically, the researchers present Mössbauer data taken on several samples of lead doped with very small concentrations of ^{119}Sn . Their results show a rapid falloff from the usual Debye-Waller behavior exhibited by solids. The results are interpreted by SSYBZ as isolated premelting around the Sn impurities, premelting that takes place at a temperature far below the bulk melting temperature of the material.

In order to do accurate Mössbauer work, it is desirable that the source Mössbauer transition be an unsplit emission line that is as narrow and has as high a recoil-free fraction f as possible. With these goals in mind, we decided to fabricate a calcium stannate ($CaSnO_3$) source. $CaSnO_3$ has a lattice structure that is simple cubic, leading to a lineshape that is both narrow and unsplit. We fabricated the Mössbauer isotope ^{119}Sn by bombarding ^{118}Sn in oxide form with neutrons at the MURR facility for approximately two months. We had previously perfected the chemistry needed to produce $CaSnO_3$ from SnO_2, checking the results using

x-ray diffraction techniques. Currently there is another $CaSnO_3$ source under irradiation at MURR that will be available for use in early summer 1992.

Another important aspect of this work was the perfecting of a technique to consistently produce homogeneous, well-characterized samples. The method of production is critical, as we must be very sure that the samples do not contain any precipitates. Moreover, the impurities must be evenly distributed throughout the sample. We are employing a methodology involving use of a Scanning Electron Microscope to ensure that our samples meet this criteria. We have suceeded in preparing uniform and well-characterized samples with long annealing and numerous checks.

As of this date, an experimental run has been completed on an annealed sample that is below the precipitation limit at room temperature. In contrast to the SSYBZ report we find no anomalous fall-off from Debye-Waller behavior at a concentration of 1.2 at. % Sn in Pb. However, in the interest of improving the thermometry and counting statistics, this is considered a preliminary result and the work is continuing. For this purpose, another $CaSnO_3$ source is currently under fabrication at the MURR facility, as mentioned above, and more Sn in Pb samples are being prepared. In addition, we are collaborating with R. Dean Taylor of Los Alamos National Laboratory for the purpose of corroborating our results and expanding the temperature range of the measurements. His latest experiments, performed on an unannealed sample with Sn concentrations of 1.6 at. % , give the same Debye-Waller temperature dependence as our annealed 1.2 at. % sample. We would conclude that the SSYBZ experiment is in error, possibly due to inhomogeneous samples. Higher concentrations of Sn above the solubility limit may well lead to sharp bends in the f(T) curve, which would be interesting as a tool for the study of precipitation, but would also invalidate the original premelting model advanced by SSYBZ.

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E. Mössbauer, Neutron Scattering, X-Ray Diffraction, and Macroscopic Studies of High T_c Superconductors Containing Tungsten

Tungsten is a unique dopant for the $YBa_2Cu_3O_{7-\delta}$ (123) high T_c superconductor in that it substitutes for copper ions and yet alters T_c by only a very small amount. The implications of this are being studied with regard to the mechanisms of high T_c superconductivity. Also, we wish to explore further the impact of these dopants on such vital parameters as the critical current J_c, which increases by a factor of two over undoped 123 with W concentration. The tungsten doped $YBa_2Cu_{3-x}W_xO_{7-\delta}$ (123-W) system has been investigated by: x-ray diffraction, neutron diffraction, resistivity, and Mössbauer spectroscopy (MS).

All 123-W samples were prepared at Purdue by our group. Samples of compositions $YBa_2Cu_{3-x}W_xO_{7-\delta}$ with $0 \leq x \leq 0.15$ were prepared from high-purity Y_2O_3, $BaCO_3$, CuO, and WO_3 powders by the usual solid-state reaction method. The stoichiometric powders were well mixed, pressed into pellets, and sintered at 950°C in air for a total period of about 100 hours with five intermediate grindings and pressings. The samples were then annealed at 500°C in an oxygen atmosphere for about 36 hours and slowly cooled.

The phase purity of every 123-W sample was checked with a standard diffractometer with Cu Kα radiation. Impurity phases were found for even low tungsten concentrations, and these peaks grow with the amount of tungsten added. The impurity peaks are identical to those reported by Bokhimi for samples prepared under similar conditions [2]. For each sample, the x-ray diffraction patterns were used to refine the unit cell parameters and the results are plotted in Fig. 1.

Three samples of 123-W doped with x = 0.04, 0.08, and 0.15 W were measured by neutron diffraction at MURR to determine their crystal structure. The neutron diffraction patterns closely resemble the x-ray patterns and show the addition of extra peaks not from the 123 structure. The results of Rietveld analysis, while not conclusive, support the model of tungsten occupancy on the Cu(1) site.

Resistance vs. temperature data were taken for each sample using a standard four-

probe device. A four-probe voltage measurement was taken across each sample for a given temperature six times, half of these with the voltage bias reversed, while a constant current of 1 mA was maintained. The resistance was obtained by averaging the six voltage measurements and dividing by the current of 1 mA. For all samples $\Delta T_c < 2$ K, and no shoulder (second phase onset) appears for W contents less than x = 0.08 W. The transition temperature of each sample was taken from the onset (10% resistance drop) of zero resistance. A graph of T_c vs. W concentration is given in Fig. 2.

Mössbauer spectra were collected for temperatures between 77.9 K and 300.5 K using the QUEGS instrument. The ^{183}W 46.5 keV Mössbauer transition was used to probe the local tungsten environment for an absorber of 123 doped with x = 0.075 W. Because of the very wide linewidth (Γ_{nat} = 1.60 cm/s), hyperfine interactions are not resolved and therefore cannot determine the site location of the doped tungsten. However, precise absorber recoilless fraction values have been extracted for each temperature by lineshape analysis techniques [5, 4, 6]. These recoilless fraction values follow the Debye model very well with a Debye temperature of 271(3) K.

While the x-ray and neutron powder diffraction patterns show that this system is not single phase, even for relatively low concentrations of tungsten, the x-ray and neutron refined unit cell parameters (see Fig. 1) suggest that the tungsten is incorporated into the 123 structure up to approximately x = 0.08 W. This suggestion is confirmed by the T_c data (see Fig. 2) which levels off at about the same tungsten concentration.

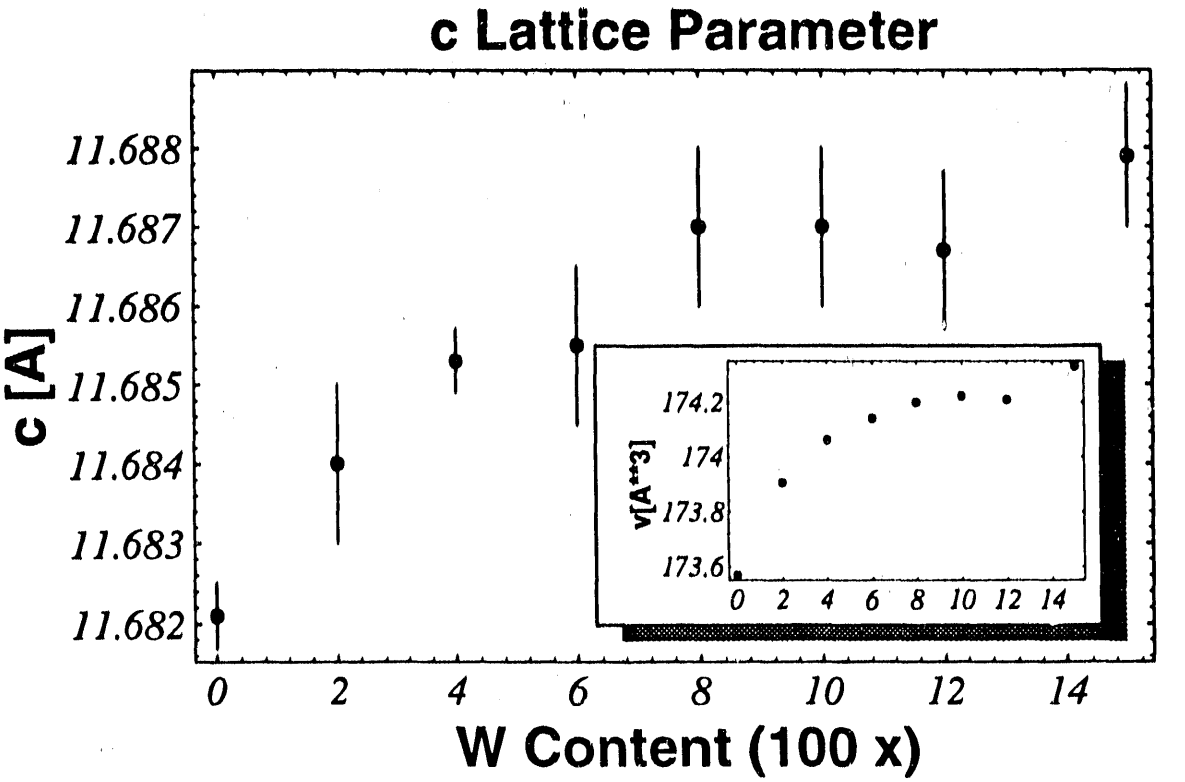
The x-ray and neutron diffraction data is similar to Bokhimi's x-ray data for samples prepared similar to ours. The most intense of the extra peaks can be attributed to the formation of $BaWO_4$. Rietveld analysis was carried out on the x = 0.15 W sample neutron data to see if the new cubic phase could be identified by assuming the dominant phase to be that of 123, a second phase of $BaWO_4$, and a third phase like Bokhimi describes. The fit is indeed better by including the cubic phase and the lattice parameter returned is the same as that reported by Bokhimi within experimental error. The intensity of the possible third phase is low, however, so no definite conclusions

about the cubic phase existence can be drawn.

The most likely candidate for tungsten to substitute is the Cu(1) chain site. The ionic radius of W^{4+} is 0.70 Å and Cu^{2+} is 0.72 Å. Tungsten may be similar to Sn^{4+} (0.71 Å) which has been shown to replace the Cu(1) chain site [1].

The Mössbauer recoilless fraction data follow the Debye model quite well. Boolchand et al. reported a softening of the lattice at $\approx$ 140 K for $EuBa_2Cu_{3-x}Sn_xO_{7-\delta}$, x = 0.021 [1]. For the temperature region examined (77.9 K - 300.5 K), no lattice softening or structure anomalies can be seen.

Identifying the tungsten site location is necessary to completely characterize the 123-W system and prove whether or not the new superconducting cubic phase proposed by Bokhimi exists. Mössbauer spectroscopy of the ^{182}W transition and neutron powder diffraction should resolve this issue.



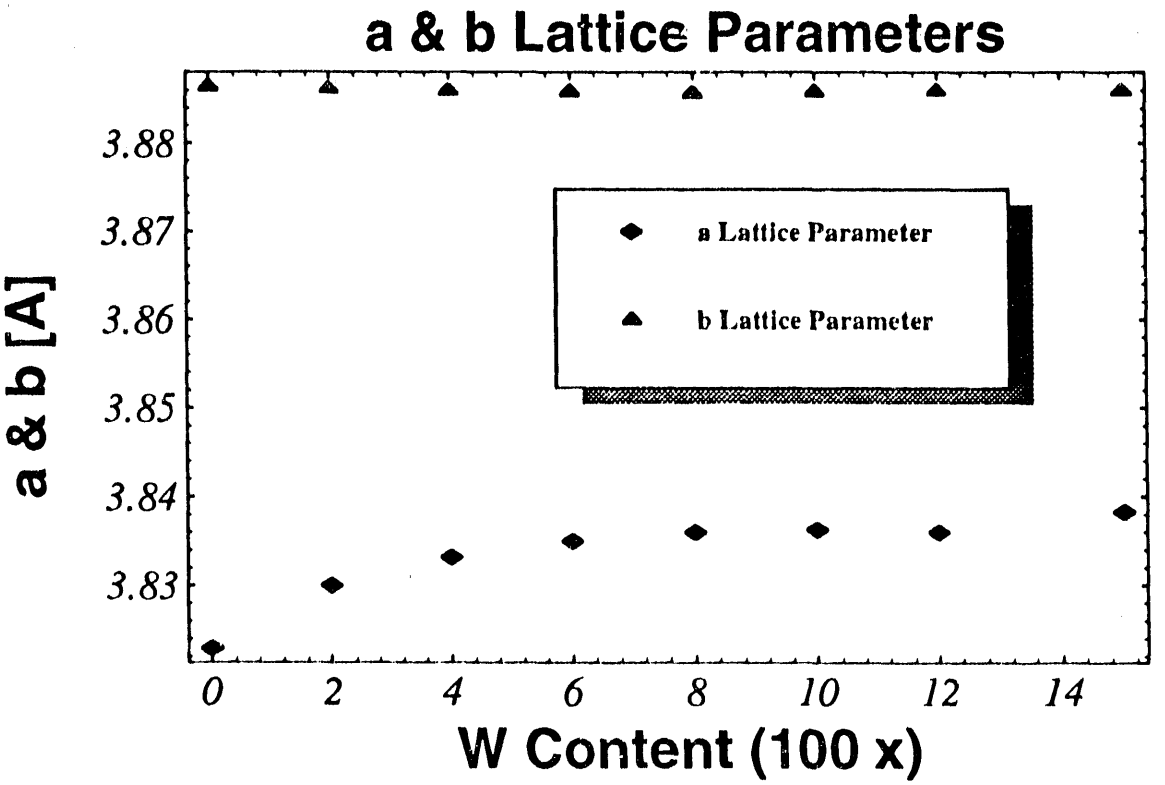


Fig. 1
The lattice parameters for samples of $YBa_2Cu_{3-x}W_xO_{7-\delta}$ with $0 \leq x \leq 0.15$.

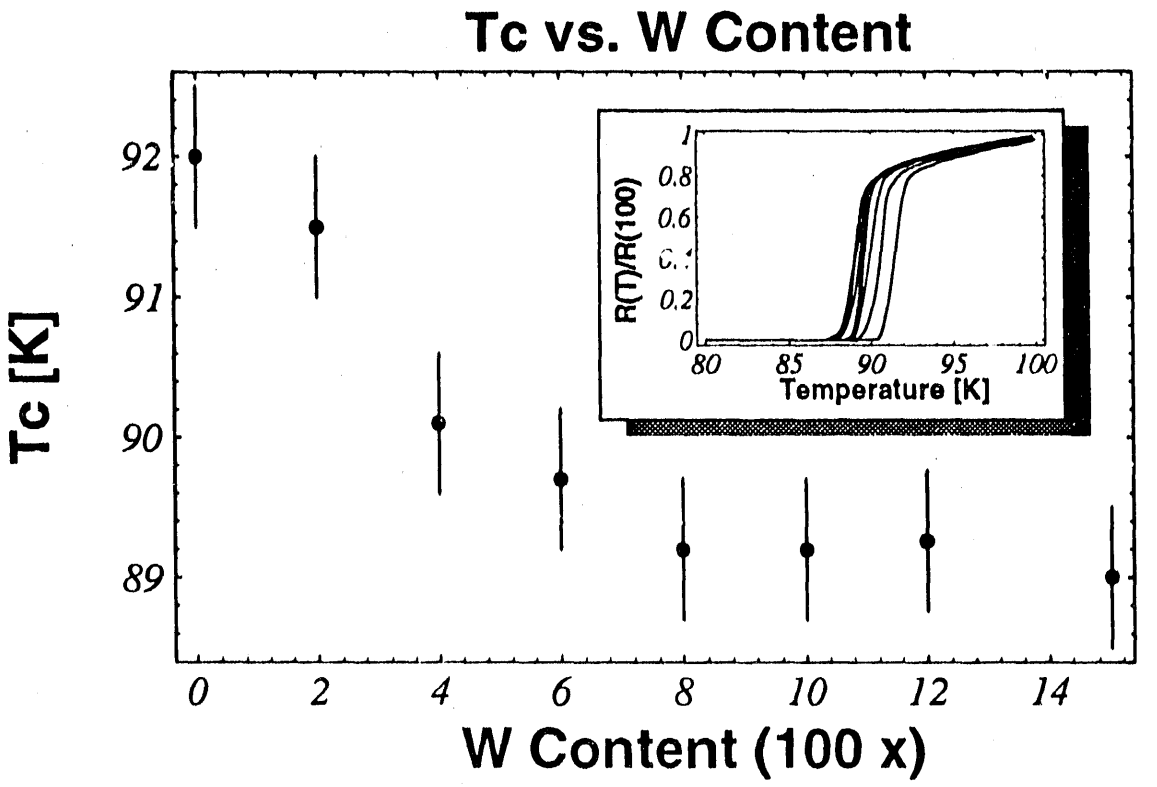


Fig. 2
The superconducting transition temperature T_c for samples of $YBa_2Cu_{3-x}W_xO_{7-\delta}$ with $0 \leq x \leq 0.15$ as measured from resistivity data.

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F. NiAl Scattering Studies

The abstract from a short manuscript (in preparation) on a "Mössbauer Scattering Experiment on the Nature of the Martensitic Phase Transition in $Ni_{0.63}Al_{0.37}$" is given below which summarizes the results of our investigations on a sample loaned by L.E. Tanner, Lawrence Livermore National Laboratory.

A recent study on $Ni_{0.63}Al_{0.37}$ has been carried out on the MURR Mössbauer gamma-ray scattering instrument. Neutron scattering has shown the presence of a "soft phonon" in the vicinity of the condensation point of the satellite peaks of the low

temperature Martensitic phase. It was thus speculated that the transition might be associated with critical fluctuations leading to dynamically broadened peaks close to T_c. The principal satellite reflection was studied over a significant temperature range from below T_c to its disappearance around 125 K. Within the resolution of the ^{183}W probe (1 μeV) the satellite reflection was found to be elastic at all temperatures indicating that any precurser peak is due to local static distortion (perhaps associated with strains or surface effects) and not to fluctuations into and out of the low temperature phase on a local basis. These results seem to confirm the current model for Martensitic transitions in which the distortions are large and discontinuous and therefore non-fluctuating.

G. Atomic Interference factors and Nuclear Casimir Effect

1. Introduction

In 1968, experiments done on ^{181}Ta by Sauer, Mathias, and Mössbauer revealed an asymmetry in the absorption of resonant photons. This asymmetry was explained as being due to final state interference effects between nuclear and electron cloud interactions, leading to a measurable interference parameter, β [1, 2, 3]. The role of β is of importance to time reversal invariance (TI) experiments where it is closely related to the time reversal interference parameter β_T (often written as ξ). Also, knowledge of β is essential in making correct isomer shift measurements in Mössbauer experiments, as its omission leads to systematic errors in the line position.

In 1964 Christenson et al. experimentally discovered that time reversal invariance (TI) was violated in kaon decay [4]. To date this remains the only known case of TI violation, despite the predictions of many theories that such a breakdown should occur in other domains of physics. One means of testing for TI breakdown in electromagnetic interactions in the nucleus is by use of the Mössbauer effect. For a E2/M1 mixed nuclear transition, we have [5, 6]

$$\frac{< f||E2||i >}{< f||M1||i >} = \pm|\delta|e^{i(\eta+\beta_T)}$$

where δ is the mixing ratio, and η is the mixing ratio phase which must be zero or some integer multiple of π if time reversal invariance is to hold. The physical source of β_T, known as the screening parameter or time reversal interference parameter, are the same final state interference effects that give rise to β, the Mössbauer interference term. What is actually measured in such TI nuclear decay experiments, is the quantity $\eta + \beta_T$, where what is needed to test for breakdown in time reversal invariance is the value of η. No experimental method has been found to measure η or β_T independently, and the practice has been to take theoretical values for β_T, and the measured values of $\eta + \beta_T$, to attain the desired η values. This limits one's confidence in the results to the confidence one has in the theory used to calculate β_T. A means of experimentally testing these theories is needed. Due to their shared physical origin, any theory that predicts a value for β_T, necessarily predicts a value for β. Though β_T cannot be determined from β, it can be directly measured, and agreement with theory would lend support to the values of β_T predicted by that theory. A particular example of this is the experiment by Gimlett et al. [7], which shows evidence for TI breakdown in the ^{191}Ir system if the theoretical value of $\beta_T = -0.0037$ [2] is used. But if the value of $\beta_T = -0.0043(4)$ [3] is used, this indication of a TI breakdown disappears. Comparison of the measured value of β to those found using two existing calculations might help indicate which, if either, should be used to interpret the results of the Gimlett work. More generally, an accurate measurement of β for any system for which the theories used in TI experiments predict a value for this quantity, would serve as a test of those theories, and could point out the need and direction for revised theoretical calculations and a reinterpretation of existing TI experiments.

Accurate values of β are also needed in Mössbauer spectroscopy since a failure to take the asymmetry produced by interference into account can introduce errors in the values of other measured quantities, particularly the Mössbauer peak position. The peak position values are effectively a measurement of the second order Doppler shift and the isomer (chemical) shift. The isomer shift provides information about the charge state of the atoms in a given material, and about

the electric field in the region of the nucleus. If the interference parameter for a given Mössbauer transition is known, then the magnitude of the asymmetry is also known and can be corrected for, increasing the accuracy of the measured isomer shifts. Similarly, measurement of magnetically split nuclear energy levels can be adversely affected by failure to correct for asymmetry effects. And yet, due to the difficulty in measuring β and the prevalence in the field for using incorrect Lorenztian lineshape equations to interpret data, few good measurements of the interference in ME systems have been carried out. One of the goals of our research has been to measure β in a variety of systems and thereby directly test the calculations of interference.

2. Standard Transmission Experiments

The majority of our interference measurements were made using the standard transmission geometry, that in which one Mössbauer absorber is Doppler shifted between a source of gamma rays and a photon detector. We generally Bragg scatter the gamma-ray beam off a monochromating crystal before it is incident on the Mössbauer absorber in order to reduce background from high energy down scatter. A schematic of this geometry is shown in Fig. 2.1. In addition to accurate interference measurements, we have made accurate measurements of natural line widths and of Mössbauer Debye-Waller factors (recoilless fraction). Our values for the recoil-free fraction have lead to Debye temperature values which differ slightly from heat capacity measurements due to a different weighting of the phonon states, so that the Mössbauer Debye-Waller temperatures supplement the heat capacity measurements.

The lineshape for this geometry is the same as that given in Sec. II, C. The transitions studied and our measured values for β are given in Table 1. All source and absorber nuclei were unsplit, single line transitions.

The interference values for the iridium and the 99.1-keV and 100.1-keV tungsten transitions, agree with the theoretical values to within error. The theoretical values for the 46.5-keV tungsten resonance however, are -0.003 [2] and -0.0028 [3], both clearly smaller than the measured value of -0.00317(6). The

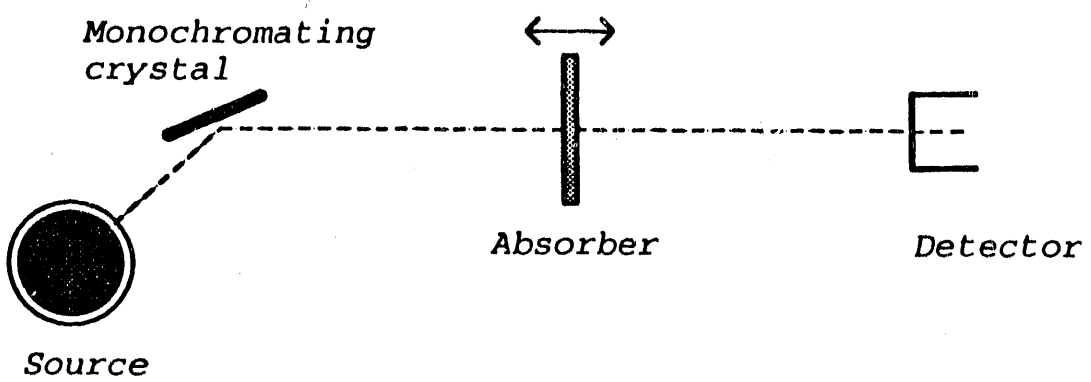

Figure 1: Schematic of the standard one Mössbauer absorber geometry

Table 1: Interference values measured using standard absorber geometry

ME isotope	transition (keV)	β	reference
^{183}W	46.5	-0.00317(6)	[8]
^{183}W	99.1	-0.013(3)	[9]
^{182}W	100.1	-0.012(1)	[9]
^{191}Ir	129.4	-0.0071(8)	[9]
^{159}Tb	58.0	-0.0058(7)	[10]

former transitions have β experiment uncertainties of 8.3% to 23%, while that for the 46.5-keV case is only 1.9%. It is possible, therefore, that the former values may also be found to deviate from theory once their accuracy has been increased to a point comparable to that of the 46.5-keV tungsten case. No published theoretical value exists for the 58.0-keV terbium transition.

The precision of the interference measurements for all these cases is sufficient to correct for asymmetry effects in most Mössbauer experiments, avoiding the problem of isomer shift distortion mentioned earlier. Our value for β in the 129.4-keV ^{191}Ir transition agrees with both theoretical calculations of β, and as such offers no insight into which, if either, theory should be used to calculate the β_T values in the Gimlett TI experiment [7]. In general, TI measurements require greater accuracy than are needed in Mössbauer isomer shift experiments. It would be desirable to add to the number of measured interference parameters for ME isotopes, which could be used by other Mössbauer researchers in their isomer shift studies. Also, it would be of value to make more accurate measurements of interference in those isotopes used in TI research, including the ^{191}Ir case presently measured to only 11.3% accuracy. Such a program of study, however, would take us too far afield of the essentially materials science focus of our DOE grant.

3. Double absorber experiment

The only clear discrepancy between a measured value of interference and the theoretical values was that of the 46.5-keV transition in tungsten. We accordingly chose to do a second experiment to help ensure that the disagreement was not due to some systematic error in the measured value. We employed two absorbers, one stationary and one Doppler shifted, as a means of enhancing the off-resonance signal and to help increase the independence of this experiment from the previous standard single absorber experiment. This geometry, originally used by Mössbauer and co-workers [11], is like conventional Mössbauer transmission geometry except that a stationary absorber of thickness number t_s is placed between the ME source and a moving absorber of thickness number t_m. A schematic is shown in Fig. 3.1.

Though the use of the stationary absorber reduces the percent effect, it also suppresses the symmetric component of the lineshape (which is maximum near E_o), hence its utility for making interference measurements whose asymmetric effects are at a maximum in regions away from E_o. The result is that the contribution of the asymmetric signal to the total lineshape can be increased over what one would get if all the absorber material were concentrated in one moving absorber. In addition, the stationary absorber's role of filtering unwanted signals from the central part of the spectrum is of use in cases where systematic errors exist which are greatest in magnitude near resonance, so that increased count statistics alone are of little value. Common examples of this are errors due to vibration or small unresolved hyperfine interactions. The transmission lineshape expression for the double absorber geometry is given by

$$C(x) = C\left\{1 - f_{so} + \frac{2f_{so}}{\pi}\int dx' \frac{e^{-t_s\mathcal{L}(2X-2u)}e^{-t_m\mathcal{L}(2x')}}{1+4X^2}\right\}, \qquad (3)$$

where

$$\mathcal{L}(2y) = \frac{1-4\beta y}{1+4y^2}, \qquad (4)$$

and we have used the dimensionless variables and other terms introduced in

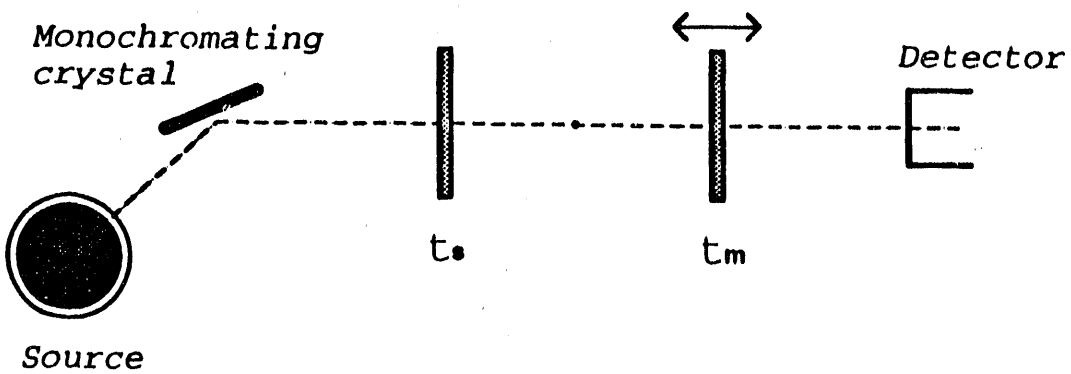

Figure 2: Schematic of the double Mössbauer absorber geometry

Sec. II, C, and $u = E_o v_{os}/\Gamma c$. In this expression v_{os} and v_{om} are isomer and second order energy shifts relative to the source, of the stationary and moving absorbers (in velocity units), respectively. Fig. 3.2. shows the characteristic "double peak" spectrum one gets for a sufficiently thick stationary absorber, even given that both source and absorber are single, unsplit transitions. The origin of the double line is that the stationary absorber has removed a greater percentage of the photons near E_o, due to its Lorentzian absorption profile, than it has from the wings. The resulting lineshape is not always a double peak, but rather depends on the thickness of t_a; smaller values result in a broadened single peak spectrum. The difference in the peak depths depend on the slight difference between the source and the stationary absorber transition energies (isomer and second order Doppler shifts), and more importantly, on the presence of a non-zero interference parameter.

Our value for interference using these method was $\beta = -0.00318(5)$ which agrees with our earlier value attained using only one absorber. We again find that the theoretical values are smaller than our measured values and outside of two standard deviations. This suggests that the current theories of atomic interference are in need of further refinement, particular since we are now able to measure these β values many times more accurately than in the past.

4. Nuclear Casimir Experiment

We have completed an experiment searching for the nuclear Casimir effect in ^{193}Ir. This was the first experimental attempt to see these cavity vacuum state fluctuation effects in nuclear transitions.

An iridium foil absorber was placed between two grounded aluminum plates. In one case the distance between the plates was 0.14 mm, in the second case the distance was 5.77 mm. The peak position was then compared for these two cases. According to a theoretical paper by Prof. Il-Tong Cheon [12], placing the Mössbauer absorber between two perfect electric conductors should result in a shift in the nuclear transition energy that would be reflected in the peak position of the Mössbauer spectra. This shift would vary inversely

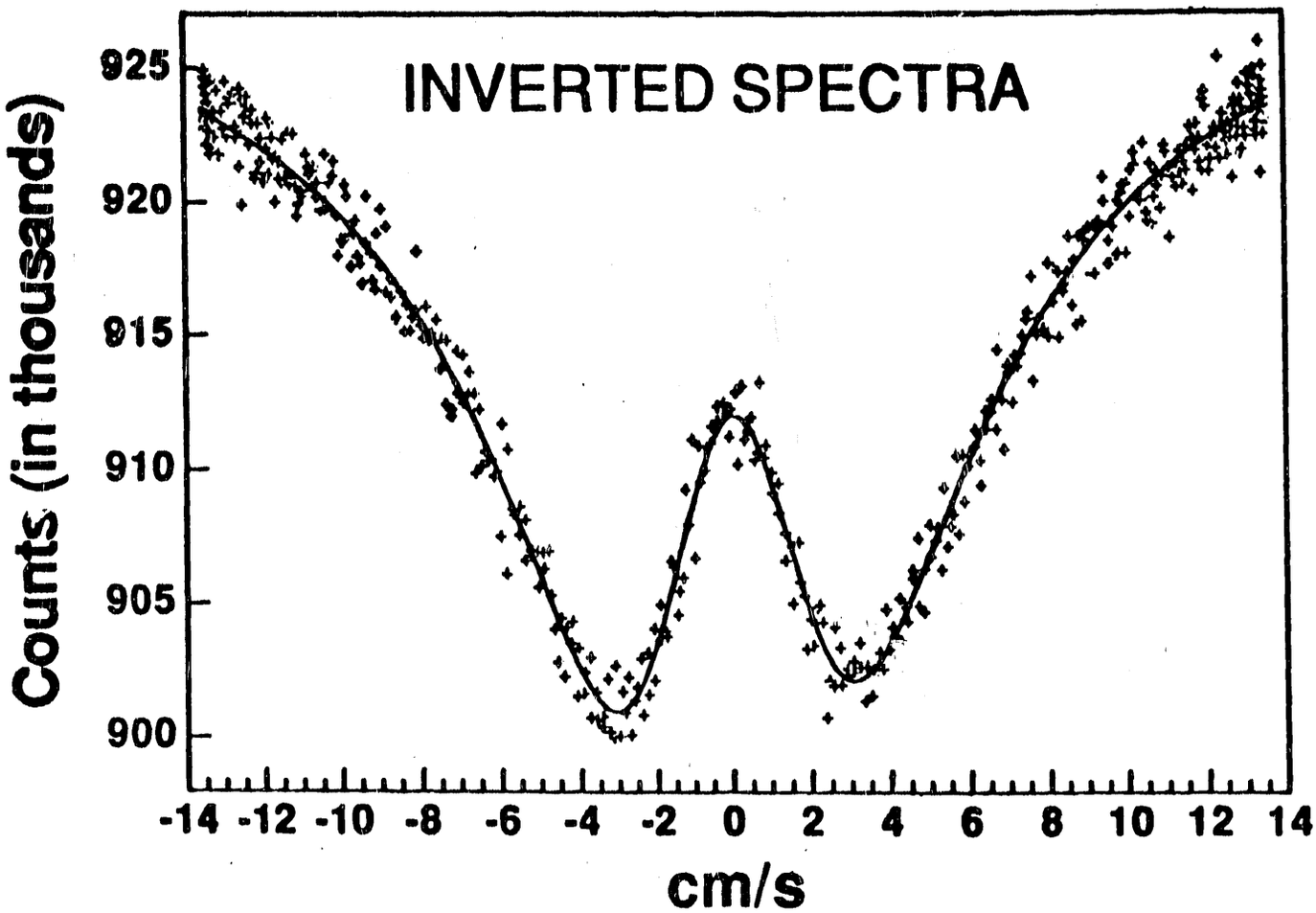

Figure 3: Double absorber Mössbauer spectra, both source and absorber nuclei are single line transitions

as the distance between the grounded plates varied. Even with a factor of 41 in the differences in the distances between the grounded plates, no shift in the peak position was observed. One possible explanation is that aluminum is not a sufficiently ideal conductor to lead to the predicted result. Since the definition of a perfect conductor is one which retains a zero internal electric field strength, it follows that no electromagnetic field (photons) could penetrate such a material. But in fact we know of no true material that is totally reflective to high energy gamma rays, whose frequency is high enough that not even superconductors can re-arrange their electrons fast enough to maintain a null internal electric field and hence prevent penetration. With this consideration, it seems that theoretical calculation based on real materials need to be undertaken which give definite predications within the range of experiment to test. We did however place an upper limit on any possible nuclear shift of 0.015 μeV for this case of boundaries made of non-ideal aluminum conductors. No further tests of this sort are currently planned until more definite predictions are available.

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III. Scattering Facilities

A. QUEGS

The QUEGS instrument consists of four main components: a radioactive source in a shielding cask with a beam line and shutter, a sample stage, a reciprocating or rotating resonant absorber, and a detector system. We show a schematic drawing of the present instrument from an earlier publication [1]. It can be thought of as the photon analog of a triple-axis neutron spectrometer in which the source is also the monochromator and the Doppler absorber in front of the detector is the analyzer. As with a triple axis, the scattering processes of interest are normally Rayleigh rather than nuclear resonant and the experiment probes $S(\vec{q},\omega)$.

As constructed, the QUEGS cask has a single beam line and a source dewar to cool sources to 80K to enhance their recoil-free fraction, f. While 80K is sufficiently low for the 46.5-keV resonance in ^{183}W used in most of our work, many other potentially useful sources, especially ^{153}Sm, require cooling to the 10 to 20K range to produce large gains in f and open new possibilities. For many studies a Bragg diffracting crystal is used as a filter to separate the monochromatic Mössbauer gamma rays from the other gamma rays in the source spectrum.

The sample stage consists of rotation, tilt and translation stages and supports cryostats, furnaces and other devices for controlling the sample environment Many of the peripherals used for neutron scattering are easily adapted for use with QUEGS.

Under most circumstances experiments are performed in a transmission (through an absorber) geometry with a Ge detector system set to window on the Mössbauer photons at the desired scattering angle ($\vec{q}$ value). An absorber is moved in front of the detector and resonantly absorbs the photons as a function of the velocity. For low velocities, a linear, oscillatory system is used and for higher velocities (liquid

quasielastic scattering studies) a rotating absorber system is employed. An alternate detector which operates in direct geometry to give a positive Mössbauer signal (rather than the negative dip observed in transmission) is a microfoil internal conversion electron (MICE) detector [2]. A cooled MICE detector was designed and built [3] to operate with QUEGS which showed significant signal enhancements [4] but it has experienced maintenance problems for long term studies, when the MICE foils must be moved. In Sec. III, D. we discuss a new approach which will eliminate this difficulty.

B. QUEGS Upgrade Completion

As discussed in our renewal request last year, a proposal was submitted to the University Research Instrument Program of DOE entitled "Multi-Beam Mössbauer Scattering Facility." Its purpose was to (1) construct a new source cask with four beam lines (instead of one), (2) incorporate a cryogenic refrigerator into the new cask such that the Mössbauer source could be cooled to 20K (instead of 80K) and (3) redesign our present cask such that the sources can be velocity modulated to allow use of a stationary MICE detector. This proposal was funded (DE FG05-91ER79044, 10/91-9/93) with $74,069 from DOE and $52,000 in matching funds from the University of Missouri and construction is underway.

The new instrument and modified (old) cask will significantly impact our future research in at least 5 principal ways. (1) It will be possible to conduct simultaneous experiments using different beam lines—hence more experimental investigations and investigators will be accommodated. (2) The ability to run simultaneous experiments will break the bottleneck of prioritizing graduate student thesis data collection periods as well as help in recruiting students who are sensitive to the present situation. (3) A new monochromating filter (MF) is being developed using a bent perfect Si crystal in transmission geometry which will allow us to take a more divergent beam from the source cask and focus it onto a point sample. This MF is based on recent successful implementation of similar monochromators at MURR for neutron scattering. By using more of the source divergence (with a wedge-shaped exit aperture) the flux on a sample can be enhanced by as much

as an order of magnitude while the angular ($\vec{q}$) resolution can be preserved by using a short source-MF distance and significantly longer MF-sample distance. (4) Cooling sources to 20K will give an extended list of useable Mössbauer sources (resonances) and hence expand the number of experiments that can be considered. (5) As mentioned earlier [3], a MICE detector can enhance the Mössbauer signal-to-continuum ratio by a factor of ten or more in favorable experiments. The most serious drawback for a MICE detector with QUEGS has been the fact that the Doppler velocities required for the ^{183}W, 46.5-keV resonance (15 cm/s) shake the cooled proportional counter and foil assembly excessively and make it too noisy for long-term operation. Modulating the sources in a re-designed cask, however, will allow the MICE detector to be stationary and let it be used to enhance the Mössbauer signal for long-term experiments.

The two biggest concerns in the upgrade for QUEGS are that no appreciable vibration from the refrigerator cold head be transmitted to the sources and that no excessive thermal leaks prevent the sources from attaining 20K or below. An early step in the upgrade process was to invite Prof. W. Steiner of the Technical University of Vienna, Austria to Missouri. He is both a well known Mössbauer spectroscopist (and Rayleigh scatterer) and an expert in cryogenic techniques. Two methods have been designed to make the thermal contact (with minimal vibration) between the source holder and the cold head. One is a straight forward connection utilizing flexible copper braids and the second is a rather complex He gas transfer arrangement with intermeshing copper cylinders 3" long with a spacing of 0.080" enclosed by a flexible welded bellows. Since the braided system has a good chance of success, however, it will be constructed and tried first since its cost will only be a small fraction of that for the transfer gas method.

In addition to technical assistance with the above problems, the consultation with Steiner has also led to a new research collaboration which will be discussed under proposed research in Sec. IV.

C. Purdue Facilities

The Purdue University Mössbauer lab has three reciprocating velocity spectrometers, two of the mechanical type and one an electromagnetic double transducer. One of our mechanical transducer systems is equipped with capability for diffraction experiments, which are feasible with ^{170}Tb sources, which decay to the Mössbauer daughter ^{170}Yb. Very small sources of this type can be prepared at the 20 Ci level and give very acceptable count rates after scattering from a single crystal specimen. This system has been designed to use with a stationary MICE [3] detector, and has in place the capacity of moving the source, and thus avoids the difficulty of moving the thin and delicate microfoils that are the heart of a MICE (microfoil conversion electron) detector.

Our current ME spectrometers are limited to liquid N_2 temperatures and above. For very energetic transitions, like the 84-keV line of ^{170}Yb, this results in a substantial reduction in recoilless fraction and observed effect. Because of these limitations DOE supported jointly with the Purdue Physics Department the purchase of $23,000 in Helium cryogenics. The equipment has been obtained from the Janice Research Corporation and is still being tested and evaluated. It has been used in our measurements of the interferences parameter for ^{191}Ir, which will soon be published.

The Purdue Mössbauer facilities included evaporators, furnaces, glove boxes, and hoods for radiochemistry. The department has a Titan mini supercomputer which facilitates the fitting of our data directly to the convolution integral, and permits precise evaluation of lineshape parameters such as recoilless fraction, isomer shift, and hyperfine interactions.

Because of interest shown by graduate students in the Purdue program, the department has expanded the facilities for carrying out our programs from two laboratories to four (each about 800 ft^2).

D. Completion of Purdue Upgrade

As an ongoing part of the upgrade begun in 1991 we plan to do the following with the funding provided by this grant:

1. Incorporate the helium source and absorber dewars into a unified framing with direct reciprocating capabilities for the continuous flow He absorber dewar. This unit will be portable and can be used for experiments carried out at Purdue, as well as special experiments involving short-lived isotopes like ^{197}Pt which need to be executed at the MURR facility.
2. The evaporator system being used was put together in the 60's and needs improved pumping capabilities for preparing MICE foils which serve as absorbers. This equipment is specified in the budget and will be paid for with equal matching funds from the Purdue Physics Department.
3. A new system for Doppler shifting our ME gamma beams by moving the monochromating crystal is planned for completion in the second year of the three year effort. Since there are serious problems in moving our heavily shielded supersources, we are developing a device for moving the monochromating crystal (LiF) along the bisector of the incident beam and the Bragg scattered beam to effect a Doppler shift in the momentum transfer. It is possible to show that this leads to a Doppler energy shift, δE, when the Doppler velocity of the monochromating crystal is V, through the relation.

$$V = \left(\frac{\delta E}{E_o}\right)\left(\frac{1}{2\sin\theta_c}\right)c,$$

where θ_c is the Bragg angle as measured in the crystal reference frame. This new technique will permit us to utilize cold MICE detectors without a need for moving the delicate microfoils in the detector and eliminate any complications due to vibration.

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IV. Proposed Research

A. Dynamics of Phase Transitions

Following the visit by W. Steiner in November 1991 in connection with design considerations of our new source cask discussed above, a scientific collaboration was begun with Steiner and a cooperative proposal on "Neutron and Mössbauer Investigations in Alloys and Single Crystals" was submitted March 1, 1992 to the Western European Programs (Austria) of NSF for travel funds associated with the proposed research (10/1/92-9/30/94). Supported by local funds, Steiner will come to MURR for July 1992 to begin these studies.

The Mössbauer scattering portion of these studies which will utilize the QUEGS instrument is concerned with the ferroelectric phase transition in lithium heptagermanate (LGO) at 283.5 K. This transition is of particular interest because both the critical slowing down characteristic for the order-disorder phase transition and the soft phonon mode characteristic for the displacive kind of phase transition have been observed [1,2,3]. Structural studies by neutron diffraction indicate that, in the paramagnetic phase, anisotropic thermal motions are present where the network of Ge-O polyhedra undergoes a displacive type of phase transition by a quenching of the tilting motion of the tetrahedra pointing to a soft mode, and that one of the two crystallographically non-equivalent Li atoms exhibits a marked anisotropy in the thermal motion. This anisotropic motion, however, can be better explained by an order-disorder model than by a displacive model, whereas the other Li atoms exhibit a "normal" behavior [4].

In the course of measurements performed on LGO by Krec and Steiner [5] with ^{57}Fe sources at room temperature at the angular range corresponding to the 009 reflection, only thermal diffuse scattering was observed supporting Pbcn as the

space group for the paraelectric phase. For the 0010 reflection at room temperature, agreement was obtained between measured and calculated dependence of the ratio of the thermally diffuse to elastically scattered radiation on the scan-length for scans below 0.7°. In the temperature interval between 250 and 355 K, the elastically scattered intensity is of the same order for the ferro- and the paraelectric phase and a distinct increase of the integrated inelastic intensity is visible. The temperature dependence of the total intensity is, with the exception of a small interval around the phase transition, very similar to the one reported for the 612 reflection [4] and points to a phase transition which is of the displacive type and is in agreement with the soft mode observed by spectroscopic investigations. The drop in intensity around the transition temperature, however, was not observed in the temperature dependence of scattered x-rays [6]. Therefore it is planned to repeat these investigations partly in the already measured temperature interval with the intense ^{183}W Mossbauer photons at QUEGS to decrease the uncertainty due to the low counting statistics of the ^{57}Fe measurements and to expand the interval to lower temperatures. The results should finally offer a better understanding of whether the character of the phase trasition has changed from the phonon to the relaxational mode.

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B. Diffusion Studies

1. Phason Hopping In AlCuFe Quasicrystals

Coddens, et al. [1] have observed quasielastic scattering of neutrons by $Al_{0.62}Cu_{0.255}Fe_{0.125}$ quasicrystals (QC) above 650° C. This broadening was interpreted as evidence for phason hopping in the icosahedral QC. The quasielastic component measured with the neutron time-of-flight spectrometer at the Laboratoire Leon Brillouin(LLB) in Saclay had a width of 95 μeV (compared with an elastic width of 77 μeV) and an intensity of 1% of the elastic component. The experimental width for elastic scattering with our quasielastic gamma-ray scattering instrument (QUEGS) at Missouri is around 8 μeV for the 46.5-keV resonance in ^{183}W. [As discussed in our various lineshape measurements, the experimental width in fact depends on the thickness of the modulation absorber as well as on the irradiation history of the source. The above value is for nominal conditions.] It therefore appears that QUEGS is very well suited for studying the phason hopping in the AlCuFe QC. G. Coddens (LLB) visited Missouri in March, 1992 and supplied us with a polycrystalline sample of the QC. Experiments on the temperature and q dependences of the quasielastic scattering (broadening) are scheduled for May and June 1992 (after R. Wagoner (Purdue) finishes his Ph.D. thesis data on interference parameter measurements). A successful investigation would help elucidate the connection between the structure and dynamics of QC.

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2. Diffusive Motions in Pb Salts

Many solids exhibit diffusive motions of the heavy ions which hop between vacant lattice sites while the cations remain stationary. In the fluorite structure (PbF_2, CaF_2, etc.) neutron scattering [1, 2] shows remarkable anisotropic diffusive scattering which is dynamic in character. In these materials the width

of the quasielastic broadening decreases rapidly with temperature, suggesting an "onset" temperature for diffusion, rather than a thermally activated process, but the neutron resolution limits the approach to zero broadening. The superior resolution of QUEGS makes it an ideal probe for these effects and will be particularly applied to PbF_2 for which the temperature (650°C) is most convenient. We would also like to extend the resolution of the neutron study by a factor of about 50 and determine if the diffusion is connected with a phase transition.

Intense diffusive scattering of neutrons in $Pb_3(PO4)_2$ near its phase transition at 800°C has also been observed by G. Coddens and M. Lambert (Orsay) at LLB. Quasielastic broadening experiments are planned by them for May 1992 to test the hypothesis that the diffusive scattering may be dynamic in origin. They have already supplied us with a polycrystalline sample and we plan initial experiments with the better energy resolution offered by QUEGS in June 1992.

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3. Orientational Disorder in C_{60}

Recent neutron scattering studies [1] of C_{60}-fullerene have shown that above the order-disorder transition temperature, T_{O-D}, at 257 K the nearly spherical C_{60} molecules are rapidly tumbling and are completely orientationally disordered. Intense quasielastic scattering is observed above T_{O-D} with line widths significantly greater than the neutron scattering resolution. Below T_{O-D} a significant diffuse scattering component remains which peaks at about 3.5 and 5.5 $Å^{-1}$. The upper peak is dominated by inelastic librational modes but the lower peak is dominated by an apparently elastic peak. We think that this is a residual orientational diffusion effect which occurs on a slower

time scale, making it too narrow to be measured with the neutron scattering probe.

The QUEGS instrument is ideally suited to these measurements since the resolution is independent of the momentum transfer and is more than 100 times finer than the neutron resolution at 3.5 $Å^{-1}$. We thus propose a careful study of the temperature dependence of this orientational diffusion below T_{O-D}. Samples of C_{60} fullerene are being prepared at Washington University (about 2 gms are needed) although the speciman studied at NIST may be available to us.

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4. Liquids

As mentioned in Sec. II, we want to do further measurements of $S(\vec{q},\omega)$ for glycerol as a function of temperature. Diffusive studies of the type performed on pentadecane (quasielastic broadening as a function of both q and temperature) [1] but with different length molecules and some different substitutional atoms will be started when time is available on QUEGS. While these studies could be very interesting when combined with molecular dynamics simulations, they are envisioned as appropriate for senior level research projects or for MS theses.

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C. Fractons in Silica Aerogels

The first neutron scattering measurements of a fracton density of states in silica gels were performed at LLB and Institut Laue-Langevin by Vacher and co-workers [1]. Although these aerogels have a density of only 0.2 g/cm^3, giving a 1/e thickness of 15 cm for the 46.5-keV Mössbauer gamma rays in ^{183}W, Coddens, Vacher (Univ. Montpellier) and Courtens (IBM Zurich) plan to provide us with a sample with a reasonable volume and thickness of 4 cm. The purpose of the planned experiments on the silica aerogel sample would be to see if the QUEGS instrument is also capable of measuring the fracton density of states and if so how they compare with neutron measurements. The main problem, assuming that the counting rates are high enough, is to determine the fall-off in scattered intensity at higher q's for different frequencies (i.e. different Doppler velocities across the Mössbauer resonance). While this experiment may have a lower chance of success than those discussed above, it would be an interesting and new application of Mössbauer scattering.

In the latter work by Vacher, et al.[2], it was suggested that there are two types of fracton dynamics in aerogels: (1) a bending type (in the floppy arms) and (2) a stretching type (in the backbone of the gels). The neutron scattering signal was predominantly from hydrogen and the two contributions were separated by the q-dependence; QUEGS on the other hand is more sensitive to the silicon. Since hydrogen is probably more prevalent in the floppy arms than in the backbone, the possibility exists that the QUEGS instrument will be able to single out the stretching modes only.

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D. Lattice Dynamics

1. Tungsten Metal

Our precision measurements of the temperature dependence, f(T), for tungsten metal between 80 and 1067K [1] opens the possibility of learning much more about the very high temperature anharmonic properties of this unique and extraordinary dense metal.

With ^{183}W foils enriched in the isotopic abundance of 183, it should be possible to make lineshape measurements up to the vicinity of 2000 K. This will require using MICE detectors in the transmission mode, which we have already shown enhance the signal-to-off-resonance counts by a factor of three for the 46.5-keV transition [2].

Such measurements would break new ground. No measurement of lattice binding have ever been carried out at such high temperatures. The anharmonic effects which are noticable at 1000 K should be very pronounced by 2000 K.

R. Shukla has carried out numerous calculations of anharmonicity in metals [3-5], and has indicated an interest in calculating the case of tungsten which he has indicated is possible to theoretically calculate.

In addition to anharmonic lattice effects, it is conceivable that diffusive effects may become significant and lead to line broadening. It would be worthy of some effort to look for these effects in tungsten, even though the temperatures attainable are considerably below melting.

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2. Tin-Doped Lead

With respect to the premelting model presented by SSYBZ it is clear that there are several alternate models that should be investigated. These include a model based on precipitation phenomena proposed by J. Mullen in an unpublished Comment on the SSYBZ paper. Due to the practical difficulties in measuring low temperature solubilities, easily measured high temperature figures are often extrapolated down to lower temperatures as needed. Thus, the lower temperature values are not well known and published values differ greatly from one another. Furthermore, the functional dependence of the precipitation rate on the temperature is not known. In general, then, there are many unanswered questions concerning precipitation phenomena in dilute alloys.

Due to our expertise in Mössbauer spectroscopy, and general facilities at Purdue University, we are in a unique position to pursue a fruitful line of research into dilute alloys. Using Mössbauer spectroscopy in condensed matter physics is advantageous because it can theoretically examine the actual physical situation at lattice sites of interest to the researcher. This methodology is especially applicable to the case at hand, for we seek to understand the exact nature of the lattice dynamics involved in dilute precipitation.

Another major advantage at Purdue is the ability to extract very precise parameters and values from the data obtained in a Mössbauer experiment through the use of an analytical representation of the lineshape using Fourier transform methodology. Our curve fitting techniques contain two distinct benefits pertinent to the current work. First, most of the curve fitting done in the field involves fitting the experimental data to a Lorentzian lineshape, which is the natural lineshape for nuclear absorption and decay, neglecting interference and saturation effects. However, in a real Mössbauer experiment there are broadening effects due to source resonance self-absorption, SRSA, and finite absorber thicknesses that are not taken into account in these simple Lorentzian curve fits. In fact, the parameters that can be extracted from the data in this manner have been shown

to give incorrect Mössbauer Effect lineshape parameters. Secondly, the values obtained for the recoil-free fraction f are calculated from absorption areas, but these are highly inaccurate for the baseline is in error when the Lorentzian fit is used. Most researchers resort to simply normalizing the areas of the absorption lines to some standard rather than reporting actual f values.

Because of the very small concentration of the Mössbauer resonant atoms, the signal vanishes quickly as the temperature rises. However, we can greatly increase the resonance signal relative to the background by using a MICE (Microfoil Internal Conversion Electron) detector. Useful for several Mössbauer isotopes, ^{119}Sn is a dramatic case. In its usual application, the MICE detector ideally counts the internal conversion electrons subsequently emitted by a fraction $\frac{\alpha}{1+\alpha}$ of the resonant Mössbauer absorptions as the beam passes through several thin foils of a material under study, where α is the internal conversion coefficient. The great signal-to-background increase that can be found in MICE experiments relative to straight transmission experiments is due to the MICE detector counting mainly resonant Mössbauer radiation with a small background resulting from photoelectrons, whereas the detector in a transmission experiment, with efficiency of course depending on the incident photon energy, registers a count for all radiation in the region of interest. Photons not belonging to the Mössbauer transition, with the exception of downscatter falling on top of the Mössbauer line, can be discriminated out electronically so that they do not appear in the data. However, they will still contribute to detector deadtime. The MICE detector is explained in great detail in a 1986 paper by J.G. Mullen et al. [1] where the authors derive the relative signal-to-off-resonance for a general case. For this research effort we can also use the MICE detector as a stationary resonance detector, replacing an ordinary detector and still realize an enhanced signal. This technique relies on the fact that not all photons emitted in the Mössbauer transition itself are zero-phonon events, and will therefore not be resonantly absorbed but will still show up in the data as background. These non-resonant photons belonging to one and multi-phonon events, of course, cannot be discriminated electronically. As stated above, the

MICE detector is relatively transparent to all but the resonant radiation, because the foils used are of very small electronic cross section compared to the resonance cross section. Furthermore, in our case ^{119}Sn has an internal conversion coefficient near 5, giving an ideal detection efficiency of 0.83 for the resonance radiation, assuming the foils are thin enough such that all of the internal conversion electrons escape. In this manner, for the extremely low concentration case under study, we can greatly increase the signal-to-off-resonance ratio thus leading the enhanced resolution for a given counting time and better f values.

In order to assess the validity of the models presented herein and as an experimental aid to check data while it is being gathered, it is desirable to know the exact Debye temperature θ_D for the lead samples under study. This involves a methodology set forth by J.G. Mullen and J.R. Stevenson [2] called the shifted absorber technique, used to obtain the results described in Sec. II, C. In subsequent Mössbauer spectra the relative positions of the lead crystal under study and the absorber are reversed, the recoilless fraction and the resonance and off-resonance intensities are measured for each case. The results will be altered between the two cases due to the crystal effectively altering the source recoilless fraction. Since the source and absorber are identical in each case, the ratio of the difference between the on and off resonance count rates for each case is the percentage elastic scattering F from the crystal. From these measurements we can find the temperature dependance of the Debye-Waller factor for pure lead as well as lead-tin alloys.

We are in a unique and advantageous position at Purdue to undertake these studies of alloying and precipitation in the tin-lead alloy system.

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E. Probe of Tungsten Doped High T_c Superconductors.

1. High T_c 123 Containing Tungsten

The ^{182}W Mössbauer transition offers an excellent opportunity to study the local environment of doped tungsten in $YBa_2Cu_{3-x}W_xO_{7-\delta}$ (123-W). The relatively narrow transition linewidth (Γ_{nat} = 1.05 mm/s) makes it possible to resolve hyperfine interactions such as electric field gradients and isomer shifts. Such measurements will allow us to determine the site locations of the doped tungsten and its valence. This technique may also be used to study 123-W with different tungsten concentrations around x = 0.08 W, in order to see if the doped tungsten favors another site after a critical concentration level is reached. Evidence of this precipitation concentration around x = 0.08 W is found in the refined lattice parameters from x-ray and neutron diffraction (see Sec. II, E.).

Samples of composition $YBa_2Cu_2WO_y$ and $Y_3Ba_8CuW_4O_{24}$ will also be examined using the ^{182}W transition. This will locate the tungsten site location and identify its valence, and will either prove or disprove the existence of the new cubic superconductor, proposed by Bokhimi. If it is proven to exist, the tungsten vibrational properties will be probed with the ^{183}W 46.5-keV transition.

Our group has had much experience with this transition and is in a unique position to fully utilize its special features. As stated before, we are able to produce a very intense mono-energetic photon beam with the QUEGS instrument [3]. This advantage in addition to the long half-live ($t_{\frac{1}{2}}$ = 115 days) of the ^{182}Ta source makes it possible to generate high resolution spectra with multi-million counts. Lineshape analyses will then be used to precisely extract the parameters we seek [4, 9, 6, 7, 10, 8].

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2. Properties of Tin-Doped Lead at Low Temperatures

While studying the lattice dynamics of tin doped in lead, we observed a remarkable broadening in the ^{119}Sn resonance below 50 K. Since lead is a cubic metal, quadrupole splittings would not be expected, especially since narrow lines were found above 50 K.

In a series of recent papers [1, 2, 3, 4], A. Overhauser has proposed that lead may contain spin density waves which affect the lattice dynamics and superconducting properties of lead. Our observation of a broadening of nearly a factor of two at 4.2 K, which falls off and becomes small in the vicinity of 50 K, may be a manifestation of such a charge density wave interacting with our small (1.6%) concentration of tin impurities. The narrowing with increasing temperature would be consistent with a motional narrowing.

Because of the exciting possibilities associated with this observation, we plan to extend and amplify these measurements. A precise determination of the temperature dependence of the width and recoilless fraction will be one of the first goals in this program. Also we need to establish that the result is independent of temperature cycling.

As Professor Overhauser is at Purdue University and is keenly interested in this problem, we will be in an excellent position to get theoretical assistance in interpreting our results.

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V. Budget

Although the diffraction Mössbauer experiments to date have been very successful and hold forth the promise of still more exciting results, the most limiting factor in progress now is manpower. At present three graduate students are being supported by this research. Ralph Wagoner is supported on Grant 45200, and Scott Dickson and John Day are supported on Grant 45199. There are three additional Purdue students, Mi Ae Park, Ji Zhang, and Carmen Shepard who are working on the project, with support from Purdue University.

MURR will give support to the Purdue students in this project as is indicated in their budget write-up. Professor G. Schupp will share in the supervision of the Purdue students who carry out research at the MURR facility.

One UMC graduate student, Ken Barnes, is working on the project and plans to terminate his studies after finishing his M.S. degree. Most of the funding sought by the principal investigator (JGM) is for the support of students and travel money to allow them to spend long stays in Columbia using the MURR facility. The funding sought is at about the same level as our previous grant from March 1, 1991 through November 31, 1991.

It should be noted that the cost of the equipment requested is being shared by Purdue University, so that for every dollar that is cut out of the budget for equipment, two dollars will be lost to the Purdue research equipment budget. Purdue's support for this project is shown by the willingness to cost share equipment, and Purdue has subsidized this project in the present and past. The Physics Department bought two computer stations for the project, has paid four months of Bruce Bullard's salary when he was finishing his thesis, and has covered fiscal year deficits since expenses have always exceeded funds granted to Purdue.

We have budgeted the cost of renting an apartment, where my graduate students and I can stay during our visits to Columbia. At this time I estimate that each of my students as well as myself will average at least two months per year at Columbia, and an apartment is cheaper (it reduces per diem charges) and superior to motels for this purpose.

We believe that our track record over the last four years is strong, and, when compared with other DOE sponsored research shows a higher productivity per dollar invested, and we believe that this warrants the appropriation of the requested funding. The large number of publications, invited talks, and Ph.D's coming out of the project all indicate a vigorous program worthy of the support level sought. The fact that the Purdue program has attracted 6 well qualified students is another evidence of the success of the program.

James G. Mullen

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EDUCATION:	University of Missouri at Rolla, B.S. in Physics	1955
	University of Illinois, M.S. in Physics	1957
	University of Illinois, Ph.D. in Physics	1960
POSITIONS:	Assistant Physicist, Argonne National Laboratory	1960-63
	Associate Physicist, Argonne National Laboratory	1963-64
	Assistant Professor of Physics, Purdue University	1964-66
	Associate Professor of Physics, Purdue University	1966-75
	Professor of Physics, Purdue University	1975-present
VISITING POSITIONS:	Visiting professor, University of California LaJolla, California	1969-70
	F.O.M. Fellow, University of Groningen, (The Netherlands)	1979-80
	Visiting Professor to the University of Missouri	1986-87

PROFESSIONAL SOCIETIES:

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American Association for the Advancement of Science
American Association of Physics Teachers
Sigma Xi
Phi Beta Pi
Tau Beta Pi
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Listed in Who's Who in America
Listed in Who's Who in Technology
Listed in Who's Who in Science
Listed in American Men and Women in Science
F.O.M. Fellow (1979-80), University of Groningen, The Netherlands
Member of the Steering Committee for ICAME '93 (International Conference on Applications of the Mössbauer Effect) Vancouver, Canada
Chairman of the Program Committee for ICAME '93

COURSES TAUGHT:

Solid State Physics, Graduate Level
Quantum Mechanics, Senior & Graduate Level
Statistical Physics, Graduate & Senior Level
Mechanics, Sophomore & Graduate Level
Thermodynamics, Senior Level
Theoretical Physics (Introduction), Senior Level
Modern Physics, Junior Level
Modern Physics Laboratory, Junior & Senior Honors
Electricity and Magnetism, Sophomore & Graduate Level
Optics, Junior & Senior Levels

RESEARCH AREA AND CURRENT RESEARCH INTEREST:

MössbauerDiffraction, General MössbauerSpectroscopy, Defects in Solids, and Mass Transport Phenomena.

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TALKS AT PROFESSIONAL MEETINGS, SEMINARS, ETC

1. Defect Studies Using the Mössbauer Effect, Gordon Research Conference, Meriden, New Hampshire, June 1964.

2. Study of Precipitation From Solid State Solution and Association of Point Imperfections by Means of the Mössbauer Effect, Fourth International Mössbauer Conference, Ithaca, New York, 1964. (Rev. Mod. Phys. **36**, 359 (1964).

3. Cobaltous Oxide (I): A Compact Single-Line Source," Mössbauer Methodology Conference, 1968.

4. The Mössbauer Effect: A New Method for Measuring Diffusion, Mössbauer Methodology Conference, 1969.

5. Mössbauer Studies of Atomic Transport in Solids and Liquids, Europhysics Conference on Atomic Transport in Solids and Liquids, Marstrand, Sweden 1970.

6. Mössbauer Study of Diffusion in Liquid Glycerol, International Conference on Applications of the Mössbauer Effect, Israel, August 1972.

7. Calibration Constants in Mössbauer Diffraction Experiments, Argonne National Laboratory, Workshop on New Directions in Mössbauer Spectroscopy, Argonne, IL, June 1977.

8. Diffusion Studies With Mössbauer Spectroscopy, University of Groningen, Netherlands, June 1979.

9. Studies of Diffusion in Solids and Liquids Using Mössbauer Spectroscopy, Technical University of Delft, Netherlands, February 1980.

10. MICE Detector Measurements in bcc Iron Above the Curie Temperature, Hyperfine Interaction Conference, Groningen, Netherlands, March 1980.

11. Mössbauer Measurements of Diffusion, Institute für Festkörperforschung, Julich, West Germany, April 1980.

12. Diffusion Studies Using Mössbauer Spectroscopy With the MICE Detector, University des, Saarland, West Germany, April 1980.

13. Diffusion Studies Using Mössbauer Spectroscopy With the MICE Detector, University of Leuven, Belgium, April 1980.

14. Diffusion Studies Using Mössbauer Spectroscopy With the MICE Detector, Mössbauer Conference, University of Nijmegen, Netherlands, June 1980.

15. Non-Lorentzian Lines in Diffusion Broadened Mössbauer Spectra, Purdue University, September 1981.

16. Measuring Highly Diffusion Broadened Lines With the MICE Detector, University of Missouri-Columbia, MO, February 1981.

17. Mössbauer Diffusion Studies: New Techniques and Recent Results, University of Delhi, Mössbauer Workshop, December 8, 1981.

18. Mössbauer Diffraction Studies, University of Delhi, Mössbauer Workshop, December 9, 1981.

19. New Frontier in Mössbauer Research, University of Delhi, Mössbauer Workshop, December 10, 1981.

20. Diffusion Studies Using the Mössbauer Effect, International Conference on Applications of the Mössbauer Effect, December 20, 1981.

21. Mössbauer Diffusion Studies, Conference on Nontraditional Methods of Diffusion, A.I.M.E., Philadelphia, October 4, 1983.

22. The Mössbauer Technique as a Probe for Studying Diffusion, University of Illinois, December 3, 1983.

23. MICE Spectroscopy and the Precision Measurement of Interference Parameters and Time Reversal Phases, Tufts University, April 26, 1985.

24. On a Possible Violation in Time Reversal, University of Missouri at Rolla, May 10, 1985.

25. Theory of the MICE Detector, University of Missouri, June 20, 1985.

26. Interference Parameters and Time Reversal Invariance, University of Missouri, June 27, 1985.

27. MICE Spectroscopy and a New Test of Time Reversal Invariance, Purdue University, September 6, 1985.

28. Quantum Interference Measurement Using Microfoil Conversion Electron (MICE) Detection, University of Cincinnati, Nov. 20, 1986.

29. Unique Signatures in Mössbauer Spectroscopy and Deconvolution of Spectra, Jet Propulsion Lab, June 10, 1987.

30. Precise Determination of Mössbauer Lineshape Parameters Including Interference, ICAME 87, Melbourne, Australia, August 16-21, 1987.

31. Mössbauer Diffraction Experiments at the Research Reactor Facility, University of Missouri at Rolla, Chemistry Department, May 2, 1987.

32. Lineshape Determination in Mössbauer Spectroscopy, The University of Missouri Research Reactor Facility, June 6, 1987.

33. Precision Determination of Mössbauer Lineshpae Parameters Including Quantum Interference, The University of Auckland, New Zealand, August 11, 1987.

34. True Mössbauer Lineshape and the Determination of Quantum Interference, Purdue University, September 3, 1987.

35. Gamma Ray Scattering, The University of Missouri University Research Reactor Facility, September 29, 1987.

36. Precision Determination of Mössbauer Lineshape and Quantum Interference, Johns Hopkins University, March 2, 1988.

37. Testing Nuclear Dispersion Theory, University of Missouri at Columbia, March 7, 1988.

38. Fourier Transform Mössbauer Spectroscopy: A New Tool for The study of Fundamental Physics, University of Texas at El Paso, May 26, 1988.

39. Using the Fourier-Transform Method of Me Spectroscopy for Precision Determination of the Recoilless Fraction, Zakopane School of Physics, May 2, 1990.

40. Measuring Recoilless Fractions and Interference Parameters Using Super-Intense Sources of Tungsten - 183, Johannes Gutenberg University, May 8, 1990.

41. Probing Fundamental Physics with the Mössbauer Effect, Purdue University, August 27, 1990.

42. Mössbauer Effect with Hundred Curie Sources, University of Alabama, Tuscaloosa, AL, March 4, 1991.

43. Precision Measurements of Recoil-Free-Fraction and Interference with Hundred Curie Sources, Stanford, CA, March 15, 1991.

44. Basic Physics and the Mössbauer Effect, Purdue University, September 02, 1991.

Approximately 40 short presentations to the APS have been given and these are not listed.

GRADUATE STUDENTS

H. N. Ok, "Mössbauer X-ray and Chemical Studies of Cobaltous Oxide," January 1968.

R. C. Knauer, "Study of Diffusion in Metals Using the Mössbauer Effect," June 1969.

J. F. Cavanagh, "Mössbauer Studies of the Transition Element Halides," June 1969.

W. R. Helms, "Studies of Nickelous and Cobaltous Oxide and Effects of n-Type and p-Type Dopants", August 1970.

A. Abras, "Mössbauer Studies of Diffusion in Liquids," August 1972.

R. L. Lindsey, "A Mössbauer Study of Self-Diffusion in Vanadium Stabilized bcc Iron," December 1975.

H. R. Anand, "Mössbauer Study of Defect Associations in Wustite and Alkali Halides," August 1976.

J. R. Stevenson, "Mössbauer Diffraction Studies," May 1981.

G. Haley, "The Influence of Nonstoichhiometry on the Verwey Transition in Magnetite as Studied by Mössbauer Spectroscopy," August 1987. (Sponsored jointly with J. Honig).

A. Djedid, "Precise Lineshape Measurement Using an Analytic Mössbauer Function," December 1987.

B. Bullard, "Mössbauer Studies in Tungsten, Iridium, and Terbium Using Line-Shape Analysis," December 1990.

CURRENT GRADUATE STUDENTS:

S. Dickson	MA. Park
J. Day	J. Zhang
R. Wagoner	C. Shepard

PAST RESEARCH ASSOCIATES OR VISITING SCIENTISTS:

C. J. Song, Research Associate

K. P. Singh, Research Associate

S. R. Hong, Visiting Professor from Korea

O. Schneeweiss, Visiting Professor from Czechslovakia

SUMMARY OF RESEARCH AND TEACHING ACHIEVEMENTS

Mass Dependence of Diffusion: (Pub.1)

This work represents the first accurate measurement of the mass dependence of diffusion in solids. The measurements showed that the rate of diffusion is less than the simple $m^{-\frac{1}{2}}$ dependence, predicted earlier from reaction rate theory. A theoretical relation for the isotope effect, $D = f\Delta K$, was proposed and it has served as a basis for interpreting the numerous follow-up experiments which have been done since. This work has received hundreds of citations and is still widely quoted in the literature.

Correlation in Anisotropic Crystals: (Pub.2,3)

The original Bardeen-Herring correlation theory was generalized to the anisotropic crystalline case, and the particular importance of correlations in anisotropic systems was first demonstrated. The work is widely cited in the literature and has been extended to the case of divacancy diffusion in alkali halides, in an important paper by R. Howard, Phys. Rev. **144**, 650 (1966).

Diffusion and Defect Studies in Alkali Halides: (Pub.4,5,6,7,8)

We were the first to demonstrate that the Mössbauer effect was a useful tool for studying the association and precipitation of defects in solids (4, 5). We were also the first to show the importance of ion size effects on diffusion in alkali halides (6). A simple model (7) was found to correlate diffusion parameters with other properties such as elastic and dielectric constants.

Thermal Aftereffects in High Recoil Mössbauer Ions: (Pub.6)

We first proposed in 1965 that it might be possible to see thermal aftereffects in Mössbauer ions produced by alpha decay or heavy ion bombardment. Numerous studies have followed up on this proposal.

Studies of the Transition Metal Oxides: (Pub.9,11,12,13,14,18,19,20,24,30)

We have demonstrated that dramatically different properties are found for stoichiometric cobaltous and nickelous oxide prepared by different methods. We explained these results by proposing another form of cobaltous oxide. Two practical results from the work were the demonstration that cobaltous oxide could be useful as an ideal unsplit Mössbauer source. Also, we showed that CoO (II) could serve as a simple means of separating oxygen and nitrogen from gas mixtures. This work is widely cited and the experimental results have led to much speculation about the defect saturated form. None of the models advanced, thus far, seem to be completely satisfactory, indicating that these studies are still ripe for further exploration.

Mössbauer Studies of Diffusion: (Pub.10,15,16,17,21,22,23,25,35,38,39)

We were the first to observe the broadening of the Mössbauer line in solid state diffusion.[10] We have also improved on the earlier measurements of diffusion in liquids by means of the Mössbauereffect. We confirmed most of the earlier theoretical predictions, but found an important breakdown in the solid state diffusion case. This work has resulted in two theoretical refinements of the earlier theory, and is also being pursued by several experimental groups.

Relaxation Phenomena: (Pub.28,29)

Our measurements (28, 29) give one of the most definitive results showing directly charge averaging in the transition metal oxides.

Diffraction Studies: (Pub.31,33,34,37,41-45)

Our studies of diffraction of anisotropic crystals with Mössbauersources has led to an important observation of a critical phenomenon associated with the transition of (1T) TaS_2 for the incommensurate to the quasi-commensurate phases. Currently, I am engaged in several projects at the University of Missouri Research Reactor dealing with diffraction.

Contributions to Instrumentation: (Pub.10,31,32,41)

We have made practical contributions to the automation of velocities spectrometers and have devised a new kind of detector (32) for measuring resonant radiation. We invented the MICE detector, and have made several recent improvements, giving greatly enhanced signal-to-background ratios. A theory of conversion electron spectroscopy was developed from comparison of MICE spectroscopy to conventional transmission spectroscopy.

Innovation in Teaching: (Pub.26,27,33)

Innovative courses based on project studies has helped many students to find self-discovery and opportunity for creativity in learning. Article on a personalized course in thermodynamics generated wide interest and promoted discussion about alternative approaches to teaching scientific material to students.

Recent Research (Pub. 41-57)

Current research of J.G.M. centers on precision determination of the lineshape parameters in Mössbauer effect (ME) spectroscopy, and the application of superintense ME sources to problems of elastic, quasi-elastic and inelastic scattering of the monochromatic recoilless photons from crystalline solids. The recent research investigations of J. Mullen can be broken into three major categories: lineshape measurements with Mössbauer transmission and microfoil conversion electron (MICE) spectroscopy, scattering experiments using superintense ME sources to study charge density waves and anharmonic effects in crystals, and the study of the discontinuities in the internal fields for very precisely characterized magnetite.

The lineshape studies, which have been recently reported, demonstrate for the first time

that precision measurements of Mössbauer lineshape parameters are possible. A new Fourier-transform method for describing ME lines has also been developed, and it has been shown that the commonly used Lorentzian function is totally inappropriate for fitting ME measurements, as it yields completely spurious lineshape parameters.

Our findings indicate that the interference parameter in every case differs by 10-20% from that predicted by theory[1] using precise relativistic wave functions. The origin of the discrepancy between theory and experiment may be due to the failure of the theory to properly include in the Hartree-Fock-Slater wave functions the effects of correlation and exchange. It is interesting that the wave functions used by Davis, Koonin, and Vogel.[1] in their calculations of these dispersion effects gave excellent agreement with regard to energy levels; however, such levels are highly insensitive to the details of the wave functions in contrast to quantum interference between resonance scattered and Rayleigh scattered photons, and between internal conversion electrons and photoelectrons.

These studies, for the first time, also make it possible to determine f(T) directly from lineshape and this offers the possibility of a new type of fingerprint in ME spectroscopy, which will prove useful to geologists and chemists. The f(T) results for ^{183}W in tungsten in etal [55-57] can be used to determine accurately cross sections and internal conversion coefficients, and to extract important nuclear information, as well as the lifetime of the state, which has not been possible in ME experiments in the past. These lineshape measurements have been shown to be equally feasible for transmission as well as conversion electron spectroscopy, and results are published in Hyperfine Interactions.[46]

The fabrication of extremely intense ME sources, in collaboration with W. Yelon and G. Shupp at the University of Missouri Research Reactor Facility, has made it possible for the first time to carry out practical scattering experiments, having the k-space resolution of an x-ray facility and the energy resolution associated with ME spectroscopy. We have demonstrated the feasibility of this high resolution ME scattering for the 46 keV transition of ^{183}W. With these high intensity sources we have been able to show that an exciting critical phenomena can be seen in tantallum disulfide just above the quasi-commensurate to incommensurate transition at 79° C. With this technique it has been possible to measure the Debye-Waller factor in the incommensurate phase and to confirm a phason temperature factor, which is independent of k. This is in marked contrast to the common Debye-Waller factor associated with phonons, which has a well-known k squared dependence.

In a third area of research on precisely prepared and characterized samples of magnetite,[50] it has been demonstrated for the first time that there is a very sharp transition in the internal magnetic field at the Verwey transition, when samples of precise stoichiometry are prepared. It has been possible to correlate these observations with recent investigations involving heat capacity, resistivity, and Seeback measurements, as well as thermal magnetic analyses of the initial permeability, and to confirm that the Verwey temperature is lowered as δ in $Fe_{3(1-\delta)}O_4$ is increased. There is a change in the Verwey transition from first order for δ less than δ_c to second order for δ greater than δ_c where $\delta_c = 0.004$.

These measurements elucidate for the first time that Mössbauer internal fields do have a sharp discontinuity at the Verwey temperature in stoichiometric magnetite; the discontinuity in the B field is very sharp and very large. This observation is counter to many years of earlier measurements in this material by a large number of Mössbauer spectroscopists, but correlates well with the recent observations in heat capacity and resistivity carried out by

Honig and collaborators at Purdue University on extremely well characterized magnetitite.

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SOME ADDED COMMENTS ON PROFESSIONAL ACTIVITIES

J.G.M. has trained eleven Ph.D.'s while at Purdue, five of whom are now tenured professors, and are active in research and teaching. His papers are widely cited in the literature and there are several fields of research that he has pioneered, such as direct observation of diffusion using Mössbauer spectroscopy, first measurement of the isotope effect in solid state diffusion, development of microfoil conversion electron (MICE) spectroscopy, and the Fourier transform method of describing and deconvoluting the Mössbauer lineshape.

He spent one year in Holland (79-80) at the University of Groningen as an F.O.M. (Fundamenteel Onderzoek der Materie) fellow. In addition to carrying out an extensive research program, he has traveled extensively and given numerous invited talks at the leading universities and government laboratories of Europe.

Recently, he returned from a one year sabbatical at the University of Missouri, at the Research Reactor Facility, which led to several important scientific breakthroughs, including a new method of analysis of Mössbauer data, giving an exact description of the line shape and showing how to deconvolute ME spectra to obtain precise recoilless fractions as well as hyperfine interaction parameters.

He is currently the Chairman of the Program Committee of the International Conference on Applications of the Mössbauer Effect, 1993 to be held in Vancouver, Candada. He is also a member of the Steering Committee which is in charge of organizing this conference.

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