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INELASTIC SCATTERING IN CONDENSED MATTER WITH HIGH INTENSITY MÖSSBAUER RADIATION

Final Technical Report
for Period December 1, 1989 - November 30, 1992

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Abstract

The QUEGS facility at MURR has 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, manuscripts submitted on alkali halides (Phys. Rev. B) and accurate Mössbauer lineshape measurements (Phys. Rev. C), and manuscripts in preparation on glycerol, NiAl and Mössbauer spectra obtained by modulating a scattering crystal. 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 Fe-57 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.

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 x 10^{14} n/cm^2 sec) and one-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 W-183 sources produced by irradiation of 100% abundant Ta-181. 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 (one week) basis as is done at MURR. The sources are cooled to 80 K 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 Tm-170, 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 four-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 20 K. This upgrade, 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 liquid and solids, and lineshape studies especially related to resonant scattering processes and lattice dynamics.

II. Progress Report

A. General Review of Progress During Last Four-Year Support Period

1. Students supported on project

Sang-Hoon Kim: Supported for two years; is now a Ph.D. student in theory.

Steve Maglic: Supported for one year; received M.S. and is presently a Ph.D. student at Northwestern University.

Ken Barnes: Supported for two years; will receive M.S. in Summer 1993 (also a H.S. teaching certificate).

Ralph Wagoner: Student from Purdue University was supported by Missouri for final year; he received Ph.D. in Summer 1992.

Raymond Law: Undergraduate student supported part-time; received B.S. in June 1992. Presently a physics graduate student at MU.

Titus Berry: Undergraduate supported part-time in 1992.

2. Honors and special achievements by principal investigators received in last four-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 Frauenfelder.

• 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 DOE.

• Group Leader, Gamma-ray Scattering, MURR.

William Yelon:

• Publication Co-Chairman, Magnetism and Magnetic Materials Conference (MMM) 1989-1991; InterMag'92 Editor.

• Oak Ridge Associated Universities (ORAU) Visiting Scholar, 1990-1991.

3. Ph.D. Theses Resulting from DOE Sponsored Research (conducted primarily at MURR).
   - Bruce Bullard, "Mössbauer Studies in Tungsten, Iridium and Terbium Using Lineshape 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.
   - Ralph A. Wagoner, "Mössbauer Spectroscopy Interference Measurements in Tungsten, Iridium and Terbium," Purdue University, August 1992.

4. List of Publications covering DOE Grant Period 1988-1992.
   1. J. G. Mullen, A. Djedid, D. Cowan, G. Schupp, M. L. Crow, Y. Cao and W. B. Yelon, "Representation of Lineshape Parameters and Deconvolution of Mössbauer Spectra," Physics Letter A**127**, 242 (1988).
   2. J. G. Mullen, A. Djedid, B. Bullard, G. Schupp, D. Cowan, Y. Cao, M. L. Crow and W. Yelon, "Precise Determination of Mössbauer Lineshape Parameters Including Interference," Hyperfine Interactions **40**, 123 (1988).
   3. J. G. Mullen, A. Djedid, G. Schupp, D. Cowan, Y. Cao, M. L. Crow and W. B. Yelon, "Fourier-Transform Method for Accurate Analysis of Mössbauer Spectra," Physical Review B**37**, 3226 (1988).
   4. G. Haley, J. G. Mullen and J. M. Honig, "First Order Change in Hyperfine Interaction at the Verwey Transition in Magnetite," Solid State Communications **69**, 285 (1989).
   5. M. L. Crow, G. Schupp, W. B. Yelon, J. G. Mullen and A. Djedid, "Temperature Dependence and Anharmonicity of the Debye-Waller Factor in Sodium Metal Using Mössbauer Gamma-ray Diffraction," Physical Review B**39**, 909 (1989).

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

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

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

9. B. R. Bullard and J. G. Mullen, Nucl. Instr. and Meth. B**51**, 198 (1990).

10. G. Schupp, B. Hammouda and C. M. Hsueh, "Quasielastic Gamma-ray Scattering from Pentadecane," Phys. Rev. A**41**, 5610 (1990).

11. B. Hammouda, G. Schupp and S. Maglic, "Quasielastic Gamma-ray Scattering from Polydimethylsiloxane in Benzene Solutions," J. Chem. Phys. **93**, 5473 (1990).

12. J. G. Mullen, B. R. Bullard and G. Schupp, "Fourier Transform Mössbauer Spectroscopy: Application to Tb, W and Ir," in: Proceedings of the Zakopane School of Physics (Poland), Vol. I, eds. J. Stanec and A. T. Pedziwiatr, (World Scientific, New Jersey, 1990), p. 18.

13. B. R. Bullard, J. G. Mullen and G. Schupp, "Mössbauer Lineshape Parameter for W-183 and Ir-192 in Metallic Tungsten and Iridium," Physical Review B**43**, 7405 (1991).

14. B. R. Bullard and J. G. Mullen, "Mössbauer Lineshape Parameters for Tb-159 in $TbAl_2$ and Tb_4O_7," Physical Review B**43**, 7416 (1991).

15. R. A. Wagoner, B. R. Bullard, J. G. Mullen and G. Schupp, "Precision Measurements of Recoil-free Fraction and Interference with Hundred Curie Sources," Hyperfine Interactions, in press.

16. R. A. Wagoner, J. G. Mullen and G. Schupp, "Double Absorber Mössbauer Spectroscopy in W-183," Physics Letters B**279**, 25 (1992).

17. M. Park, P. A. Polstra and J. G. Mullen, "Analytic Representations of the Mössbauer Recoil-less Fraction, Debye-Waller Factors, Lattice Energies and Heat Capacities," submitted to American Journal of Physics.
18. R. A. Wagoner, J. G. Mullen and G. Schupp, "High Intensity Gamma-ray Scattering from Alkali Halide Crystals," submitted to Physical Review B.
19. R. A. Wagoner, J. G. Mullen and G. Schupp, "Accurate Mössbauer Lineshape Measurements Including Interference in W-182, W-183, Ir-191 and Tb-159," submitted to Physical Review C.
20. G. Schupp, W. B. Yelon and R. Law, "Mössbauer Scattering Experiments on the Nature of Martensitic Phase Transition in $Ni_{0.63}Al_{0.37}$," in preparation (to be submitted to Solid State Communications).

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 Lineshape Parameters Including Quantum Interference, ICAME'87, Melbourne, Australia, August 16-21, 1987.
   5. Precise Determination of Mössbauer Lineshape Parameters Including Interference, ICAME'87, Melbourne, Australia, August 16-21, 1987.
   6. True Mössbauer Lineshape and the Determination of Quantum Interference, Purdue University, September 3, 1987.
   7. Gamma-ray Scattering, The University of Missouri 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 8, 1992.
9. Mössbauer Scattering Studies with High-Intensity Sources, Utah State University, April 8, 1992.
10. Mössbauer Scattering Studies with High-Intensity Sources, University of Missouri, September 9, 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, $\Delta\varepsilon/\Gamma$, 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

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

where $\Delta\varepsilon$ 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 from the slope is 122 Å. This value is much larger than 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

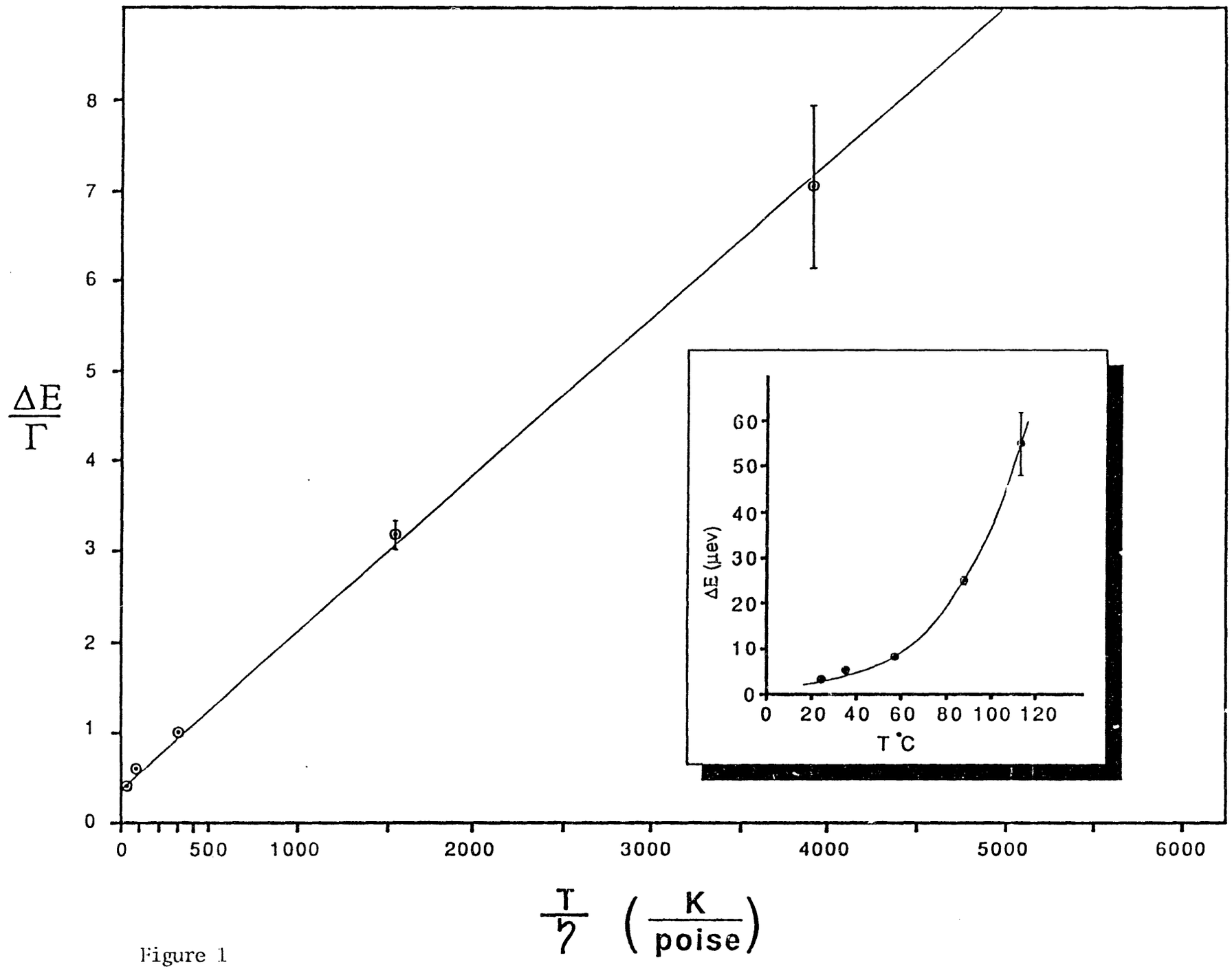
ΔE/Γ
0
1
2
3
4
5
6
7
8
0
500
1000
2000
3000
4000
5000
6000
T/η (K/poise)
ΔE (μev)
0
10
20
30
40
50
60
0
20
40
60
80
100
120
T °C

Figure 1

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. These data will be presented at the ICAME'93 meeting in Vancouver, B.C., August 1993.

References

1. K. P. Singh and J. G. Mullen, Phys. Rev. A6, 2354 (1972).
2. K. S. Singwi and A. Sjölander, Phys. Rev. **120**, 1093 (1960).
3. R. A. Wagoner, private communication.

C. Gamma-ray Scattering from Alkali Halides

We have successfully 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 Ta-183 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 Mössbaue transmission experiment, and the count number C is given by

$$C(x) = C_o\left\{1 - f_{sb} + \frac{2f_{sb}}{\pi}\int dx' \frac{e^{-t\mathcal{L}(2x')}}{1 + 4(x' - x)^2}\right\} \qquad (1)$$

where

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

and we have made use of the dimensionless variable $x = (E_o v/c - E_r)/\Gamma$ and $x' = (E - E_o)/\Gamma$. The Doppler velocity of the analyzer is v, E_r is the difference in transition energy between the Ta-183 source nuclei and the W-183 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

$$f_{sa} = \left(\frac{\varepsilon}{\varepsilon + 1}\right) f_{so} \quad ,$$

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 εN, and the number inelastically scattered, with energy still within the discriminated energy window centered about 46.5 keV, is given by iN. 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 equation we have,

$$F = \frac{f_{sa}}{f_{sb}} = \frac{\varepsilon}{\varepsilon + i} \quad . \tag{2}$$

By least squares fitting to the before and after case, we arrive at values for fsb and fsa, 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 $F = f_s/f_b$

	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 coefficient of i/e we obtained the values shown in the last column of the table displaying $F = f_s/f_b$. 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 value of O'Connor and Butt [2]. These earlier experiments were done with Co-57 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 Fe-57 experiments which require months or years for much lower accuracy. This work has been submitted for publication (See Sec. A4, #18).

References

1. J. G. Mullen and J. R. Stevens, in: Workshop on New Directions in Mössbauer Spectroscopy (Argonne 1977), ed. G. Perlow, American Institute of Physics Press, p. 55-57.
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 integrations 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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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.

The data are 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.

References

1. B. R. Bullard, J. G. Mullen and G. Schupp, Phys. Rev. B**43**, 7504 (1991).

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 $0 \le x \le 0.15$ 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 CuKα 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 W-183 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.

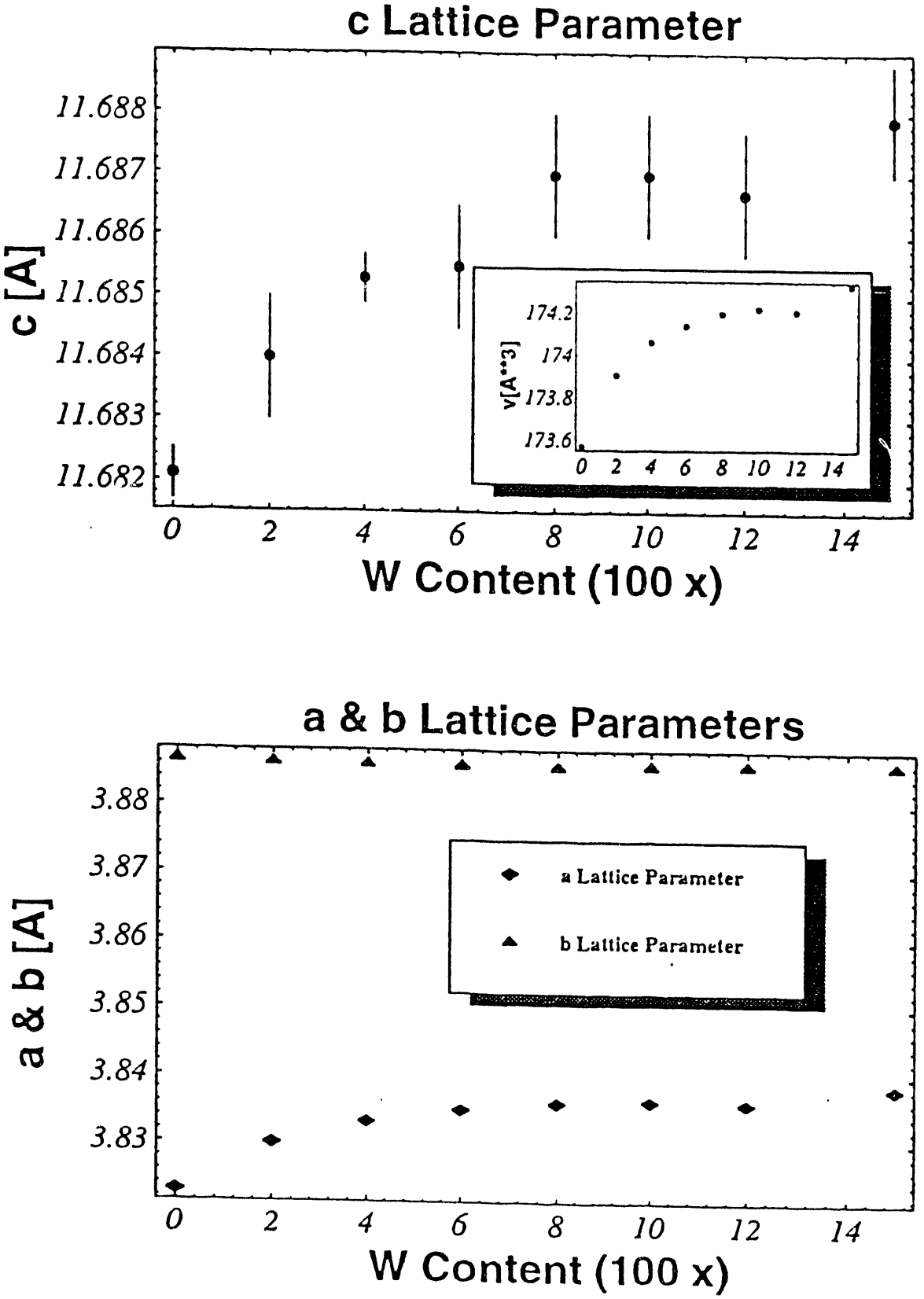

Figure 1
The lattice parameters for samples of $YBa_2Cu_{3-x}W_xO_{7-\delta}$ with $0 \leq x \leq 0.15$.

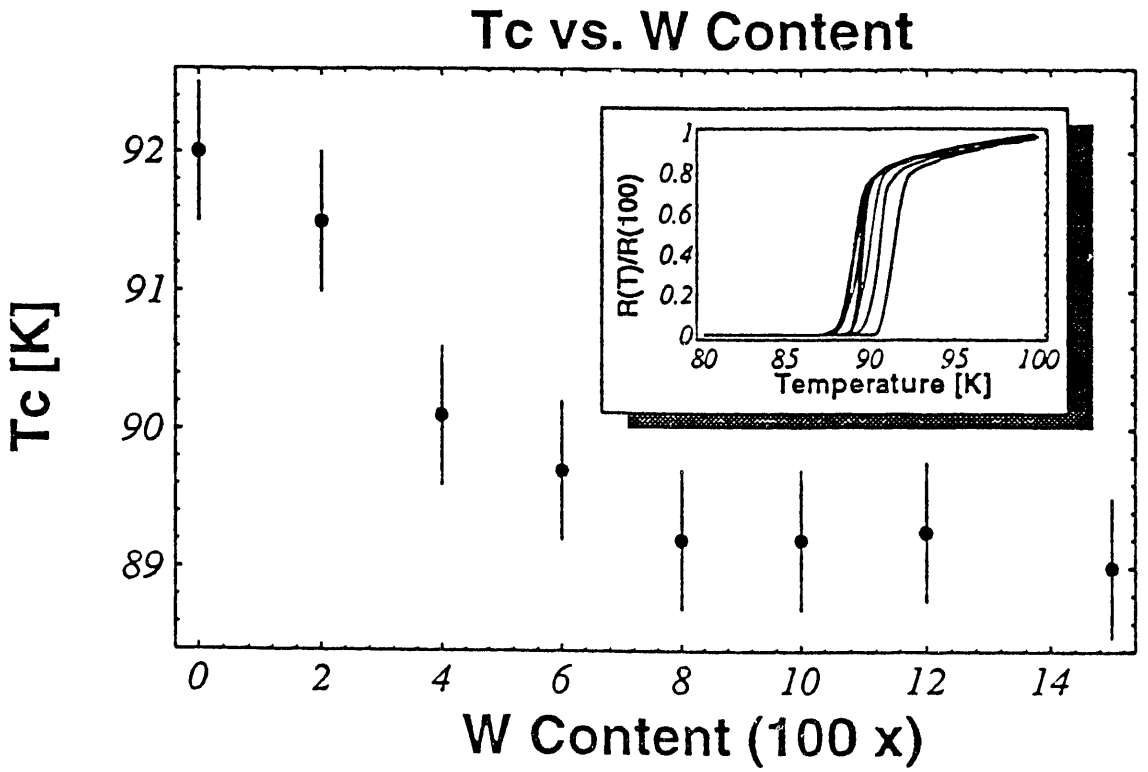

Figure 2
The superconducting transition temperature T_c for samples of $YBa_2Cu_{3-x}W_xO_{7-\delta}$ with $0 \leq x \leq 0.15$ as measured from resistivity data.

The x-ray and neutron diffraction data are 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 0.070 Å and Cu^{2+} is 0.782 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 ≈ 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 W-182 transition and neutron powder diffraction should resolve this issue.

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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 $Ni_{0.63}Al_{0.36}$ 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 W-183 probe (1 μeV) the satellite reflection was found to be elastic at all temperatures indicating that any precursor 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 Ta-181 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 [1-3]. 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 an E2/M1 mixed nuclear transition, we have [5,6]

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

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 Ir-191 system if the theoretical value of β_T = -0.0037 [2] is used. But if the value of β_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 Lorentzian 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

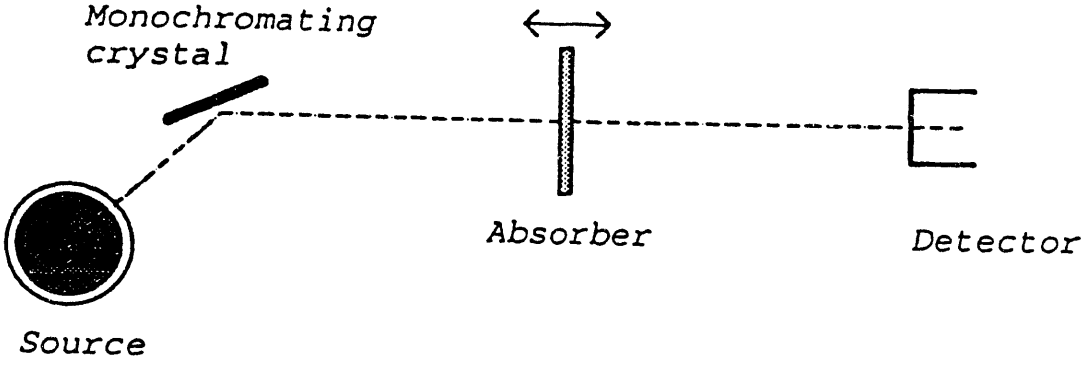

Fig. 2.1: Schematic of the standard one Mössbauer absorber geometry

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 int rference 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 former transitions have β experiment uncertainties of 8.5% 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.

Table 1: Interference values measured using standard absorber geometry

ME Isotope	Transition (keV)	β	Reference
W-183	46.5	-0.00317(6)	[8]
W-183	99.1	-0.013(3)	[9]
W-182	100.1	-0.012(1)	[9]
Ir-191	129.4	-0.0071(8)	[9]
Tb-159	58.0	-0.0058(7)	[10]

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 Ir-191 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 Ir-191 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

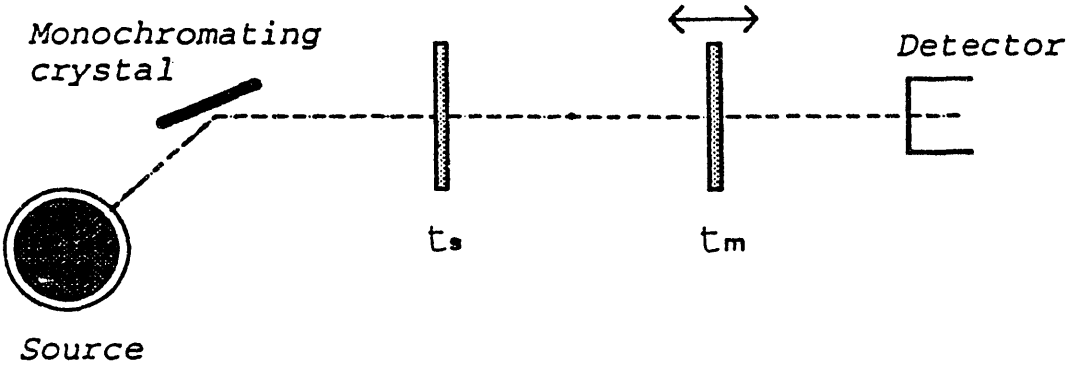

Fig. 3.1: Schematic of the double Mössbauer absorber geometry

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

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

where

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

and we have used the dimensionless variables and other terms introduced in 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. Figure 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_s; 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 methods 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

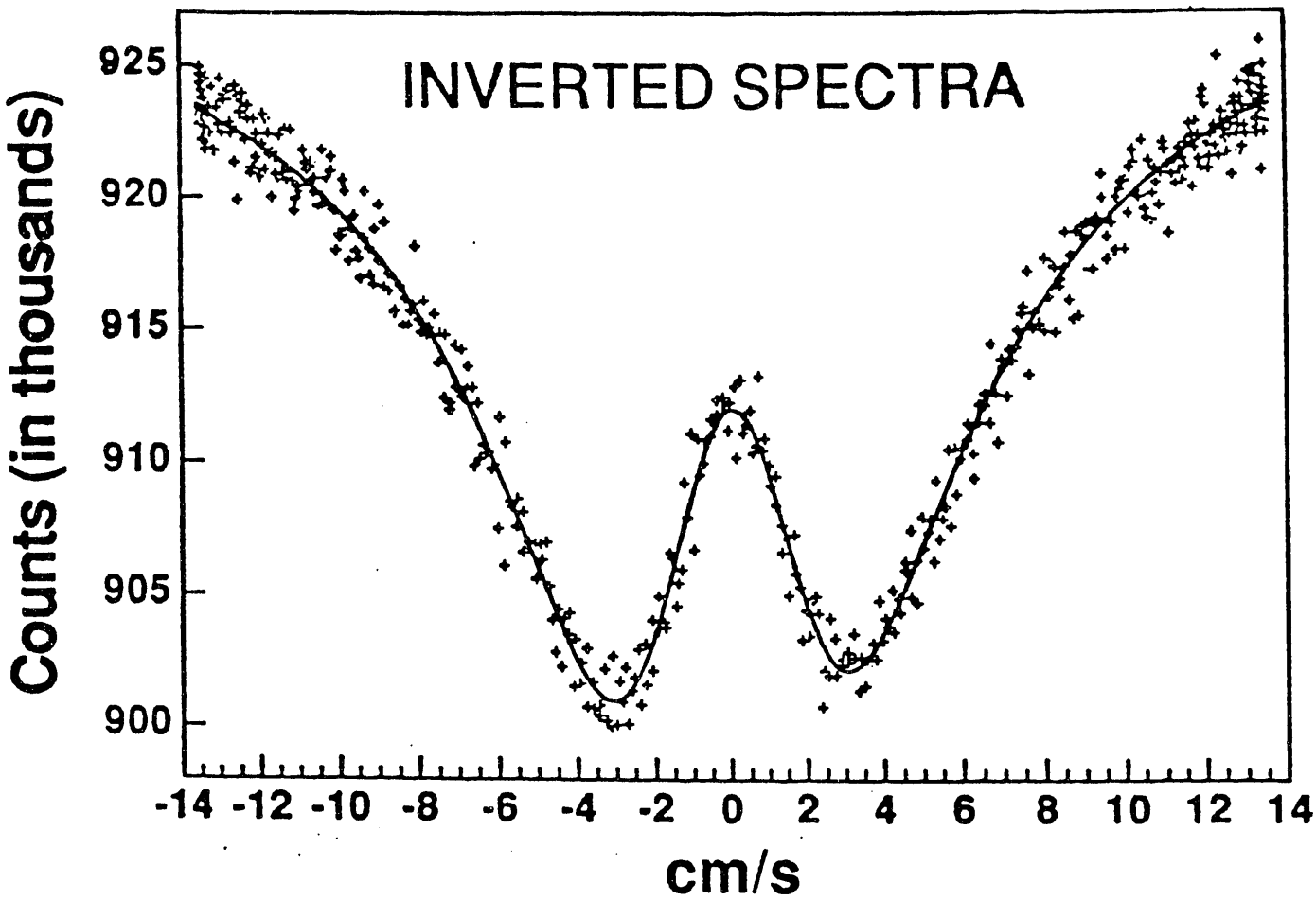

Fig. 3.2: Double absorber Mössbauer spectra, both source and absorber nuclei are single line transitions

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 Ir-193. 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 those 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 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 needs to be undertaken which gives definite predication 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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H. New Technique for Obtaining Mössbauer Velocity Spectra

In most of our studies with the QUEGS instrument at MURR, a LiF crystal is used to Bragg reflect the Mössbauer gamma rays of interest to give a "pure" beam. The gamma rays are, of course, already quite monochromatic so we refer to this as a filtering crystal rather than as a monochromator. The new technique that has been demonstrated is to obtain the velocity modulation needed for a Mössbauer spectrum by oscillating the filtering crystal along the Q-vector for the Bragg scattering. Figure 1 shows the experimental arrangement where the amplitude of the oscillation for the crystal, A, is 0.50 cm. The oscillation is provided by a crank where the maximum linear velocity for the crystal is 15 cm/s. Simple considerations show that the Mössbauer Doppler components along the incident and reflected beams are $v\sin\theta$, giving a measured line with Γ_m equal to $\Gamma/2\sin\theta$, where Γ is the usual Mössbauer width and θ is the Bragg angle for the reflection used.

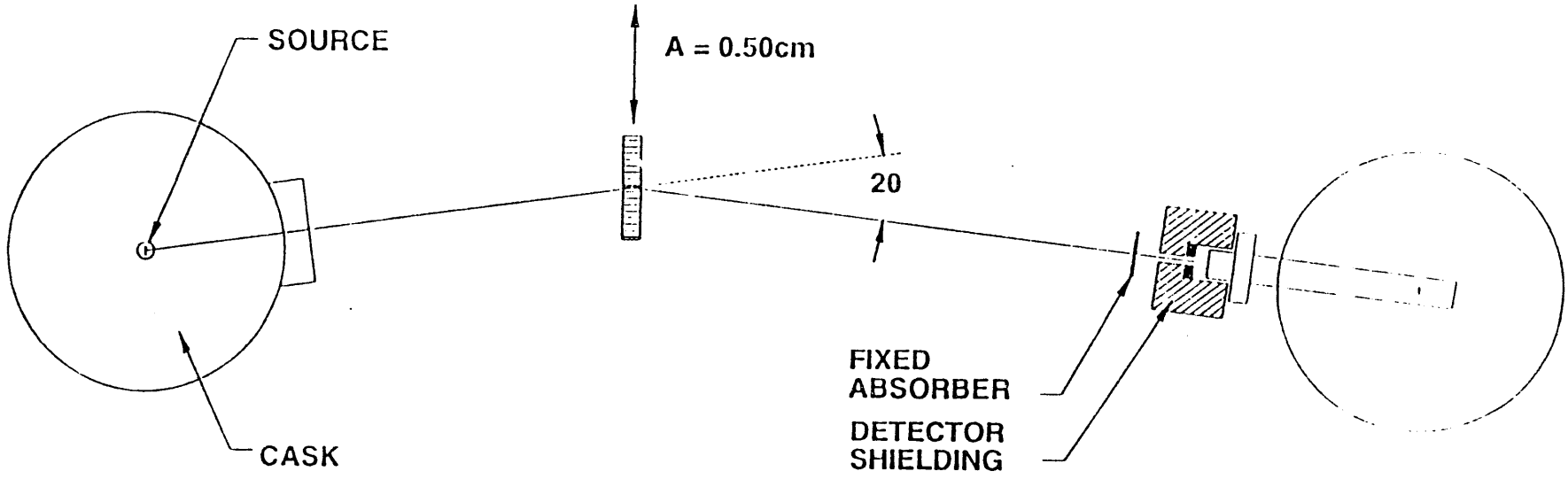

Fig. 1. Schematic drawing for the source, oscillating monochromating filter crystal, fixed absorber, and Ge detector arrangement used in these measurements. A is the amplitude of the oscillatory motion.

Figure 2A shows the multiscaling spectrum obtained with the 400 Bragg reflection for the 46.5-keV photons from W-183 with source, W absorber and Ge detector all at rest. Figure 2B shows the usual spectrum obtained by oscillating the absorber along the scattered beam line. Figure 2C summarizes the measured linewidths versus the expected widths for the four Bragg reflections used.

The principal application for this technique will be in conjunction with the MICE detector developed earlier [1]. For the 46.5-keV resonance, Γ is 1.6 cm/s and the MICE detector must be oscillated at rather large velocities which causes it to become electronically noisy. By oscillating the filtering crystal (which is always needed with the MICE because it does not afford energy discrimination), the source, sample and detector (absorber) are all at rest. Figure 3 shows the multiscaling spectrum obtained with the MICE for the 400 Bragg reflection from the oscillating crystal. It demonstrates the larger signal-to-continuum ratio obtained with the MICE detector for favorable transitions. These data will be presented at the ICAME'93 meeting in Vancouver, B.C., August 1993.

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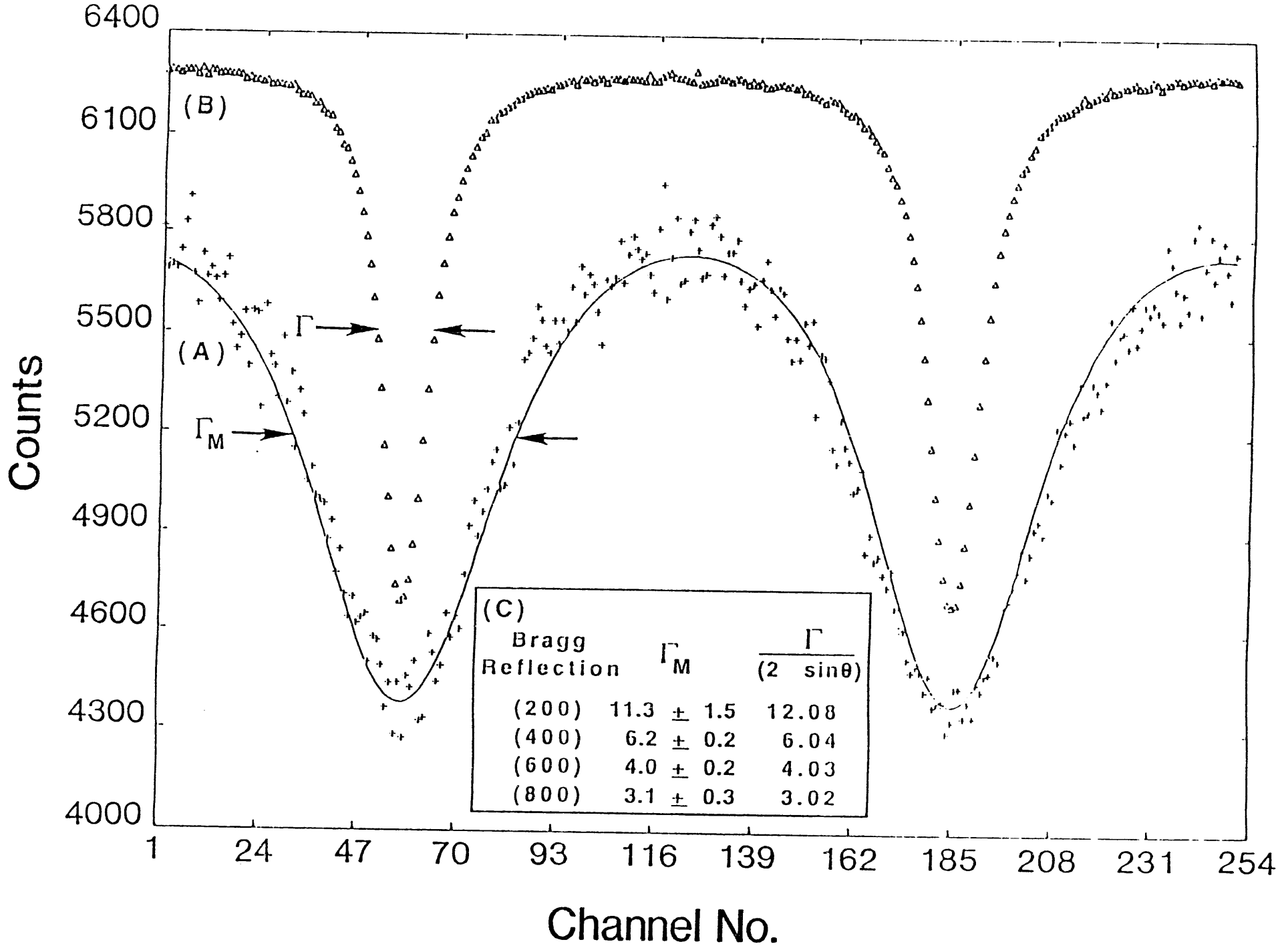

Fig. 2. (A) Multiscaling spectrum taken with the experimental arrangement shown in Fig. 1. (B) Spectrum taken with the monochromating crystal fixed and the absorber oscillated along the scattered beam line. (C) Summary of the observed line widths in cm/s versus the expected widths for the four Bragg reflections used.

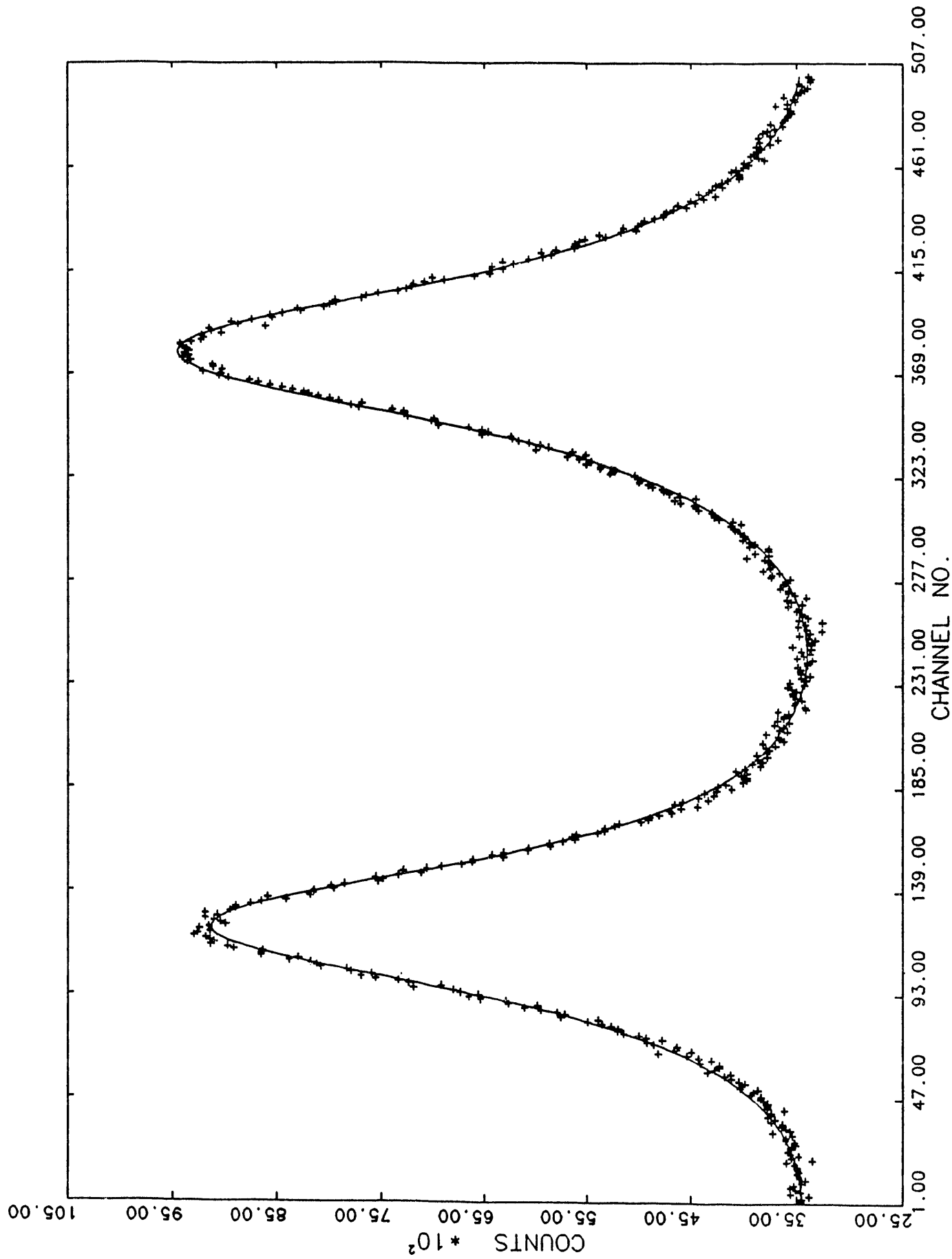

Fig. 3. Multiscaling spectrum taken with the experimental arrangement shown in Fig. 1 where a MICE detector replaced the fixed absorber and Ge detector. Γ_m in this case was 6.09 ± 0.03 cm/s.

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