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Mössbauer effect in ^{67}Zn

D. Griesinger, R. V. Pound, and W. Vetterling
Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138

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Nuclear-resonance absorption has been observed with an enriched ^{67}ZnO absorber, and with sources of ^{67}Zn diffused into ZnO, ZnS (both wurtzite and sphalerite), ZnSe, ZnTe, and Cu. Resonance was also observed with a copper host and a natural crystal of sphalerite. The apparatus, capable of handling count rates exceeding 2×10^5 counts/sec, could detect resonances of 0.01% depth in the life of a single 10 mCi source. Variations in the integrated areas of peaks in the ZnO-ZnO spectrum are explained by inhomogeneous electric field gradients. Isomer shifts cover a range of 112 μm/sec, and are found (expect for the metallic Cu host) to be linear in lattice spacing. The sign of this relation suggests that the excited-state charge radius exceeds that of the ground state. Calculations show the shifts to be primarily of chemical origin, with only small contributions from the second-order Doppler shift associated with zero-point motion.

INTRODUCTION

The 93-keV level in ^{67}Zn, with 9.1-μ sec half-life, was recognized early in the development of applications of recoil-free nuclear resonance (Mössbauer effect) as holding the promise of providing an electromagnetic resonance of extraordinarily small fractional width ($\Gamma_0/E = 5 \times 10^{-16}$). Attempts were carried out to observe that resonance before chemical and physical properties of sources and absorbers were recognized as contributing significant energy shifts. The failure of the earliest trial reported[1] was attributed to the probable presence of shifts inherent in different zero-point energies of lattice oscillators in sources and absorbers, resulting in no absorption at zero relative velocity, even in the absence of hyperfine structure. The earliest successful experiments with ^{67}Zn used chemically identical sources and absorbers, and magnetic splitting was employed to expose the resonance.[2-4] The absorptions found (at 4 °K) were very small (0.3%) and the line shapes were not directly observable.

Alfimenkov *et al.*[5] observed partially resolved spectra of 0.2% depth (uncorrected for background) using a quartz transducer as a Doppler spectrometer with a velocity range of about ±12 μm/sec. The source was a deuteron-irradiated foil of baked natural ZnO and the absorber was ZnO, enriched to 33% in ^{67}Zn. Fully resolved quadrupole hyperfine spectra of ZnO were reported by de Waard and Perlow,[6] and by Beskrovny, Lebedev, and Ostanevich.[7] Both groups used Doppler spectrometers based on stacked-quartz transducers and multiscalars. Perlow, Potzel, Kash, and de Waard[8,9] have used ZnO single-crystal sources in which the ^{67}Ga parent was generated *in situ* by deuteron bombardment. Sintered polycrystalline ZnO, enriched to 89.6% in ^{67}Zn, was used as the absorber material. Their best main line, centered at zero relative velocity, had about 1% depth and a full width at half-maximum of 0.75 μm/sec. This width is greater than the width derived from the 9.1-μ sec lifetime only by the factor 2.4.

We have carried out experiments with a variety of source matrices. One objective was to find sources and absorbers with cubic structures that might lead to further improvements in the energy resolution.

EQUIPMENT

The velocity spectrometer utilized a commercially available cylinder of PZT-4 (lead zirconate-titanate),[10] with $\frac{1}{2}$-in. o.d., $\frac{1}{2}$-in. length, and $\frac{1}{32}$-in. wall thickness (Fig. 1). A sinusoidal voltage of up to 340 V peak-to-peak, at frequencies up to 400 Hz, was applied between the inner and outer surface electrodes. The resulting elongation and contrac-

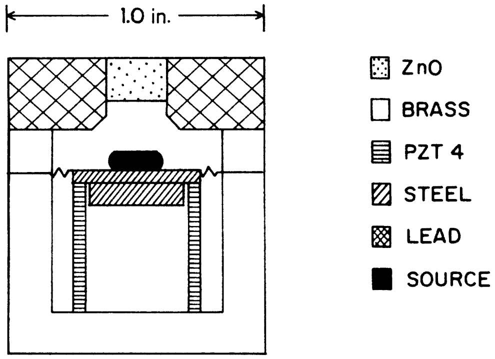

FIG. 1. Transducer assembly containing PZT-4 cylinder and spring loaded end-cap.

tion of the cylinder, at 4 °K, provided sinusoidal velocity modulations up to 225 μm/sec between the source and absorber. The source was mounted with silicone grease to a steel end-cap on top of the PZT cylinder. The end-cap was kept in contact with the cylinder by a concentrically ribbed Be-Cu diaphragmatic spring which exerted a room-temperature force of about 1.5×10^6 dyn. The PZT cylinder was contained inside a brass housing which held the diaphragm and absorber in position.

In most cases the absorber was a pill containing 1.94 g/cm^2 of ZnO enriched to 89.7% of ^{67}Zn, obtained from Oak Ridge National Laboratory. The powdered material was compressed and heated to 1100 °C for 6 h, followed by cooling at 30 °C/h. This pill was pressed into a lead disk which was mounted on the brass housing just above the source. The temperature of the transducer could be easily monitored by measuring the change in capacitance of the PZT cylinder as the assembly was cooled.

The upper limit of modulation velocity was set by the voltage limit for reasonably linear response of the PZT material, and by the rate of channel advance available with a Northern NS600 multichannel analyzer. The minimum dwell-time per channel was 20 μsec. At the maximum sweep range used, only 128 of the channels were available for the full cycle, giving a resolution averaging about 7.5 μm/sec per channel. In order to eliminate dead-time losses at high rates of channel advance, a buffer memory with a capacity of ten counts was incorporated into the multichannel analyzer.

Radiation from the source was detected with a NaI detector, using a wide-band amplifier and a high-speed single-channel pulse-height analyzer to discriminate the 93-keV γ rays. With an aperture of $\frac{1}{2}$-in. diameter at a distance of 2 in. from the source, the count rate inside of the analyzer window at 93-keV was initially over 2×10^5 counts/sec. Thus, about 7×10^{10} counts were available during the life of the source. An electromechanical counter kept track of the number of times the seventh channel of the multichannel analyzer passed 10^6 counts. The finite pulse-pair resolution time of 0.5 μm reduced the observed absorption by about 7% at an average count rate of 1.4 $\times 10^5$ counts/sec.

SOURCE PREPARATION

The source material was carrier-free ^{67}Ga obtained from a commercial supplier[11] as a solution of $GaCl_3$ in 0.1*N* HCl. It was provided with specific activities up to 1250 mCi/ml, but typically 200 mCi/ml. Acceptable results were often attainable by simply depositing the $GaCl_3$ on the host and diffusing without regard to the fate of the chlorine. Various attempts to remove the chlorine by electroplating or chemical processing were unrewarding.

The hosts were prepared in most cases from powders which were compressed and, if possible, sintered. The sintered pills contain adequate free volume to allow easy absorption of the active solution. The process described was a problem for the silicon and zinc telluride hosts. The brittle silicon grains would not form a coherent pill, and instead were heated to near melting for 30 min with a hydrogen torch while in an evacuated quartz tube. Zinc telluride demonstrated a strong tendency to sublime and recrystallize in the coolest available location.

The heat treatment for diffusion in each pill was different, being based on diffusion data when it was available. Temperatures were chosen to give diffusion to a depth of at least several μm in a time short (typically 5 to 10 h) compared to the 78-h source life. The source was cooled slowly at a rate of 30–50 °C per h for about half of the sources.

The various materials differed in their ability to retain the gallium during diffusion. Zinc oxide pills retained all of the activity even though diffusion proceeded in air at 1100 °C. Copper also retains the activity well, and could be heated in an atmosphere of flowing hydrogen. Diffusion was performed for the other materials in sealed quartz capsules, usually evacuated. The high surface area of the sintered pills (compared to the surface area of the capsule) tended to retain the majority of the activity, even for a material such as silicon which was very similar to quartz. The capsule also prevented loss of the source material through sublimation, which was important for zinc telluride and zinc selenide. The zinc telluride that sublimed to the cooler end of the capsule and recrystallized was worth retaining, since it tended to have high specific activity.

Beskrovny *et al.*[7] reported stronger resonances from zinc oxide sources which had been cooled very rapidly, and we used this technique for the zinc sulfide, zinc selenide, and one of the zinc oxide sources. We found with zinc oxide that rapid cooling gave wider but not significantly deeper lines than a slow cool.

RESULTS

There were a number of source-absorber combinations for which no lines were found at the limits of isomer shift, statistical accuracy, and velocity resolution investigated (Table I). In the number of channels indicated, each velocity was swept through twice, once with positive and once with

TABLE I. Runs in which no lines were observed.

Source-absorber	Detector aperture (in.)	Analyzer channels	Velocity range (μm/sec)	Counts channel
Al(^{67}Ga) vs ^{67}ZnO	$\frac{1}{2}$	256	±135	64×10^6
	$\frac{1}{2}$	128	202	90
	$\frac{1}{2}$	128	270	95
	$\frac{1}{2}$	256	101	59
	$\frac{1}{2}, \frac{5}{8}$	256	135	301
	$\frac{7}{8}$	128	270	360
Si(^{67}Ga) vs ^{67}ZnO	$\frac{5}{8}$	256	135	209
	$1\frac{1}{4}$	128	270	271
ZnS(^{67}Ga) vs ZnS(nat)	$\frac{3}{4}$	512	14	37
Cu(^{67}Ga) vs Zn(nat)	$\frac{3}{4}$	512	45	28

negative acceleration.

Success was experienced with a ^{67}ZnO absorber, used with the following sources: ZnO, cubic ZnS (sphalerite), hexagonal ZnS (wurtzite), ZnSe, ZnTe, and copper. A line was also obtained with the ^{67}Ga in copper, with an absorber made from a natural crystal of ZnS. The results of these runs are shown in Figs. 2–4, and the parameters are given in Table II. Velocities are relative to the enriched ZnO, with a negative isomer shift indicating that the source must be moved away from the absorber to achieve resonance. Isomer shifts were determined only visually in recognition of uncertainty in the absolute value and constancy of the transducer calibration. The lines are broadened several times beyond their natural Lorentzian width (in part from the finite solid angle and large velocity offsets), and the absence of independent knowledge of detailed line shapes counteracts the increased accuracy seemingly available from computer fitting.

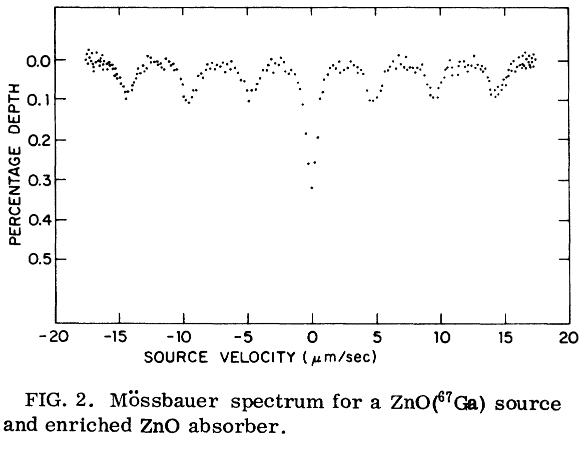

FIG. 2. Mössbauer spectrum for a ZnO(^{67}Ga) source and enriched ZnO absorber.

DISCUSSION

There is sufficient statistical accuracy in the ZnO-ZnO data to note a significant variation in both the amplitudes and the integrated areas of satellite lines. For example, if the satellites in Fig. 2 are labeled No. 1 to No. 6 from left to right, it is found that peaks No. 2 and No. 4 have integrated areas approximately 30% larger than the other

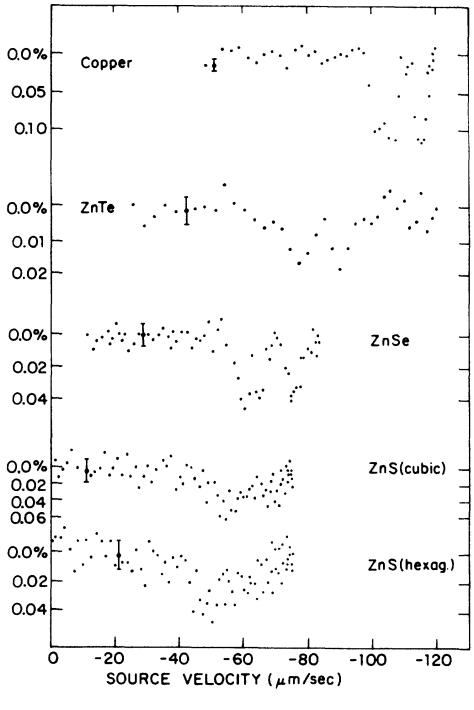

FIG. 3. Mössbauer spectra for sources of ^{67}Ga in copper and zinc chalcogenide lattices. The absorber for all spectra is ZnO, enriched in ^{67}Zn.

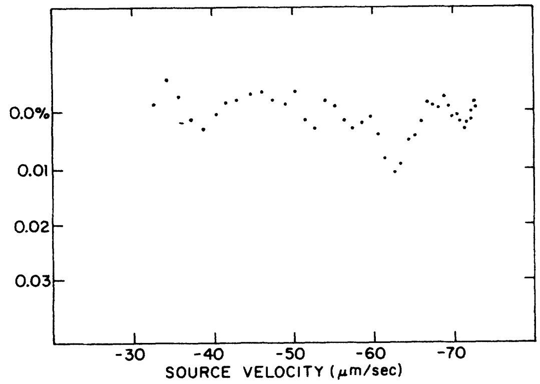

FIG. 4. Mössbauer absorption for a Cu(^{67}Ga) source, and natural sphalerite crystal absorber. The data has been smoothed by averaging each point with the average of its two neighbors.

peaks. These variations are presumed to be due to a nonuniform distribution of the ^{67}Ga parent throughout the source crystals, and to an inhomogeneous electric field gradient. In an inhomogeneous electric field gradient, the transitions involving the $\pm\frac{1}{2}$, $\pm\frac{3}{2}$, and $\pm\frac{5}{2}$ excited-spin substates are broadened in the ratio 4 : 1 : 5 respectively. In some locations, a fraction of the $\pm\frac{1}{2}$ and $\pm\frac{5}{2}$ nuclei may be shifted entirely from their respective lines, while the spin $\pm\frac{3}{2}$ nuclei are only moderately affected. If this happens in the source, as we suspect for the data presented here, then lines No. 2 and No. 4, which involve the level in the source with spin component $\pm\frac{3}{2}$, will exhibit larger integrated area.

The ZnO source which was quickly cooled showed similar variations in the sizes of the satellites. The central line of the ZnO-ZnO spectrum is about three times wider than $2\Gamma_0 = 0.32$ μm/sec. The line shapes of the satellites appear to be nearly Gaussian. The ZnO source was used with both a thick and a thin absorber in an effort to determine the f value of the source and absorber. The nonuniform broadening made interpretation of the data difficult, but the f value of both the source and the absorber appears to be about 0.013 ± 0.003.

The wurtzite (hexagonal ZnS) source was prepared by heating sphalerite (cubic ZnS) powder in an evacuated quartz capsule for 6 h at 1000 °C followed by very rapid cooling. The structure was determined by x-ray diffraction after the activity had decayed. The same heat treatment with an atmosphere of sulfur vapor inside the capsule followed by slightly slower cooling (10 min) produced sources which retained the sphalerite structure.

Wurtzite sources contain an electric field gradient different from that of ZnO, and the absorption spectrum with a ZnO absorber should be complex. Thus we expected that wurtzite would produce a broad resonance. However, the Mössbauer resonances with wurtzite and sphalerite sources were extremely broad and shallow. The broad resonance produced by the sphalerite source may indicate that it was a mixture of the two crystal forms. The isomer shifts for the two forms were measurably different.

ISOMER SHIFTS

The number of isomer shifts now available makes it possible to speculate on the systematics involved. The γ ray energy and resolution of the ^{67}Zn resonance are such that not only chemical effects but also, to an unusual degree, differences of zero-point motion could produce shifts many times the linewidth. Pound and Rebka have estimated that the zero-point energy of $\frac{9}{8} k\theta_D$ per atom would lead to a second-order Doppler shift of $\langle -v^2/2c^2 \rangle = (-15$ μm/sec$)\Theta_D/M$, where M is taken to be the average host mass. This formula approximately describes

TABLE II. Line parameters.

Source host matrix	Absorber	Counts/channel (units of 10^6)	Isomer shift (μm/sec)	Observed depth	Observed FWHM[a] (μm/sec)
ZnO	^{67}ZnO	60	0.0 ± 0.05	0.33%	1.0–1.6
ZnS (wurtzite)	^{67}ZnO	115	-50 ± 4	0.03%	23
ZnS (sphalerite)	^{67}ZnO	48	-54 ± 4	0.05%	19
ZnSe	^{67}ZnO	250	-66.4 ± 1	0.05%	3.7
ZnTe	^{67}ZnO	522	-82 ± 3	0.02%	6.3
Cu	^{67}ZnO	116	-111 ± 3	0.13%	4.2
Cu	ZnS(nat)	707	-63 ± 3	0.01%	3.3

[a] FWHM, full width at half-maximum.

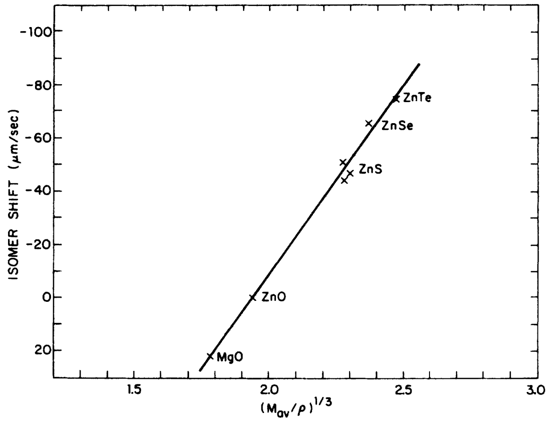

FIG. 5. Experimental isomer shifts as a function of lattice spacing. The isomer shift for MgO was taken from Ref. 7.

the relative shifts experimentally observed in ZnO, ZnSe, ZnTe, and to some degree ZnS. It makes significant errors for MgO,[7] and copper hosts, and predicts a shift between a natural ZnO source and enriched ^{67}ZnO absorber which is precluded by the data.

Exact computer calculations in one dimension, for both monatomic and diatomic hosts, show the zinc chalcogenides, and MgO as well, to be much less differentiated by the zero-point motion than the above approach predicts. The calculations recognize that kinetic energy is not shared equally by the two species in a diatomic lattice, nor is it the same for host and impurity atoms in an otherwise monatomic lattice. The MgO host had to be treated as a special case due to the existence of three atomic species (Mg, O, Zn), and a remarkably high Debye temperature. The results are consistent with an extension of arguments proposed by Lipkin[12] for the three-dimensional case, but applicable only to monatomic hosts. The extension involves only the use of the average host mass for diatomic lattices as the analogue of the host mass in a monatomic lattice.

The zero-point vibration calculations yield much smaller shifts than are observed experimentally. Consequently the isomer shifts for the group of compounds chosen appear to be largely chemical in nature. A linear relation was found between the measured isomer shifts and tabulated values of interatomic spacing for the zinc chalcogenides. The relation extends to MgO if the spacing parameter is instead chosen to be $r \equiv (M_{av}/\rho)^{1/3}$, where ρ and M_{av} are the host density and average atomic weight, respectively. The experimental data, corrected for the small shift due to zero-point motion (as derived from the one-dimensional calculations and the results of Lipkin[12]), are plotted as a function of r in Fig. 5.

A linear dependence of isomer shift on lattice spacing has been noted for other classes of semiconductors. Hafemeister and de Waard[13] found such a dependence for both substitutional and interstitial ^{129}I in diamond, silicon, and germanium. A similar relation was noted by Weyer *et al.*[14] for substitutional and interstitial ^{119}Sn in diamond, silicon, germanium, and α-tin. Both groups of data were discussed in more detail and given a theoretical interpretation by Antončík.[15] It is interesting that for both isotopes, the substitutional and interstitial nuclei had linear dependences on spacing with slopes of opposite sign.

In our Mössbauer studies, the radioactive nuclei were diffused into the host, and occupied primarily substitutional sites. Such impurities may respond to the lattice spacing both through compression (due to restricted volume), and through the charge transfer of the chemical bonds. The zinc compounds are bonded with 4*s* electrons. If one speculates that larger lattice constants are associated with less ionic bonds, then larger lattice spacings imply higher 4*s*-electron density at the zinc nucleus. The observed sign of the variation in the isomer shift with r then implies that the charge radius of the excited state is greater than that of the ground state. The data from the copper host also predict a larger charge radius for the excited state. We expect the electron density at the ^{67}Ga nucleus in copper to be larger than that in any of the zinc chalcogenides, since the 4*s* wave functions are only slightly distorted, at the zinc sites, by their participation in the conduction band. This high electron density is observed to produce the largest negative isomer shift with respect to a ZnO absorber.

We are continuing these experiments with metallic materials in the hope of finding a definitive example which demonstrates the role of zero-point motion as a line-shifting mechanism.

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