Mössbauer Effect for Fe⁵⁷ in Beryllium, Copper, Tungsten, and Platinum†

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The Mössbauer effect has been studied for Fe⁵⁷ as an impurity in Be, Cu, W, and Pt. The positions of the resonances and the ratios of recoilless fractions at different temperatures were determined. The behavior of these quantities as a function of temperature indicates the approximate correctness of the simple expectation that the impurity should behave as if it were in a solid composed only of the impurity atoms with a Debye temperature given by $\Theta_{\text{eff}} = (M_{\text{host}}/M_{\text{impurity}})^{1/2}\Theta_{\text{host}}$.

I. INTRODUCTION

THE Mössbauer effect offers an experimental technique for investigating certain problems concerning the dynamics of crystal lattices. First, there is the thermal shift[1,2]

$$\Delta E_\gamma = -\tfrac{1}{2}E_\gamma\langle v^2\rangle/c^2,$$

where v is the velocity of a nucleus emitting or absorbing recoilless gamma rays. Secondly, the recoilless fraction is given by

$$f = \exp[-\langle(\mathbf{k}\cdot\mathbf{r})^2\rangle_T],$$

where $\mathbf{k}$ is the wave vector of the emitted or absorbed gamma ray and $\mathbf{r}$ is the displacement of the interacting nucleus from its equilibrium position in the lattice.

The behavior of an isotropic harmonic lattice consisting of only one kind of atoms can be represented by the Debye model. Then $\langle v^2\rangle$ and $\langle r^2\rangle$ can be evaluated, and from these the thermal shift and the recoilless fraction can be calculated. The computation of these quantities becomes vastly more complicated when impurity atoms are considered. There are now many theoretical papers which deal with the problem of impurities.[3-11]

On the experimental side, it is possible to measure changes in the position and intensity of Mössbauer resonances as the temperature is varied. These changes can then be interpreted as changes in the mean-square velocity and in the mean-square displacement of impurity atoms. In the present work we have sought to measure changes in $\langle v^2\rangle$ and in $\langle r^2\rangle$ as a function of temperature for the case of Fe⁵⁷ nuclei in various other metals. These metals were chosen as host materials for the sake of convenience and to obtain a wide range of atomic masses and of Debye temperatures.

Soon after the discovery of the Mössbauer effect, it was suggested that the recoilless fraction could be enhanced by incorporating the nuclide in a lattice of high Debye temperature. Indeed, one of us (J.P.S.) incorporated some radioactive Os¹⁹¹ in Be, but found no indication of any resonant absorption. In a discussion, W. Marshall remarked that one should not expect such an enhancement. Since the Debye temperature is proportional to the cutoff frequency in the phonon spectrum, one might expect it to vary inversely as the square root of the mass of the impurity atom. Although the Debye model is likely to be a rather crude approximation for describing an impurity in a lattice, the use of an effective Debye temperature

$$\Theta_{\text{eff}} = (M_{\text{host}}/M_{\text{impurity}})^{1/2}\Theta_{\text{host}} \tag{1}$$

should provide a better approximation than the assumption that the Debye temperature for the impurity is the same as for the host. More recently several authors[3,10] have put this expectation on a more quantitative basis. Their work indicates that in the region covered by our measurements this expectation should be valid if the forces between the impurity atom and the host atoms are similar to those between the host atoms themselves.

II. EXPERIMENTAL PROCEDURE

A. Velocity Drive

The Mössbauer resonances were observed by the usual method of measuring the counting rate for gamma radiation as a function of the relative velocity between source and absorber. The source, contained in an appropriate cryostat, was mounted on the carriage of our Monarch EE lathe. The absorber, clamped inside a vacuum furnace, and the scintillation detector were mounted on the lathe bed. The required velocities were provided by moving the carriage to and fro at a constant speed by means of the lead screw. This apparatus and

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TABLE I. Preparation of sources. In the heat treatment the Be and Cu sources were brought up to the final temperature in an atmosphere of hydrogen. All sources were treated in a high vacuum.

Metal	Dimensions (in.)	Method of depositing Co^{57}	Heat treatment Temperature (°C)	Time (hours)
Be	1.0 diam×1/16	electroplating	750	20
Cu	1.0 diam×0.0005	electroplating	800	2
W	½×½×0.001	evaporation	700	3
			800	3.5
			950	2
Pt	½×½×0.0005	evaporation	700	0.08
			800	1

the associated procedures have already been described[12] in greater detail.

B. Sources

Each source was prepared by depositing Co^{57} onto a disk of the host metal. The Co^{57} was then diffused into the host metal by heating the disk in a hydrogen atmosphere. Subsequently each source was annealed in a hydrogen atmosphere, which served to reduce any oxides. Finally, any hydrogen absorbed in the metal was driven off by further heating in vacuo. Details of the source preparation are given in Table I.

C. Absorber

For an investigation of the properties of Mössbauer sources, it is best to use an absorber that has but a single absorption line. We were fortunate in that we had such an absorber available in the form of enriched metallic Fe^{57} foils which were heated to $10° \pm 1°$ above the Curie temperature of 770°C in a vacuum furnace.[12]

The measured linewidth of such an absorber is about

0.4 mm/sec, and at resonance it absorbs over 65% of the recoilless gamma rays.

D. Method of Measurement

Each source was investigated at three different temperatures: $T_1 = 82$, $T_2 = 298$, and $T_3 \approx 425$°K. These temperatures were obtained by filling the source cryostat with liquid nitrogen, water at room temperature, or mineral oil kept hot by an immersion heater, respectively.

The absorption line was traced out by measuring the counting rate of 14-keV photons at 20 to 25 different preset speeds. Thus 40 to 50 points on the absorption spectrum were obtained in a velocity range from -8.0 to $+8.0$ mm/sec. In order to compensate for drifts in the scintillation detector, the spectrum was traversed twice in each run, first going from low to high speeds, then from high to low speeds. Typical resonance curves are shown in Fig. 1.

III. RESULTS

A. Analysis

Each resonance curve thus obtained was fitted to a Lorentzian line shape by means of a least-squares program on the IBM-704 computer. This analysis yielded values for the fractional depth α, the width β, the position $S(T)$ of the absorption line, and the probable error in each of these quantities. It is assumed that only the statistical error in the measured counting rates is significant in producing these probable errors. The results are given in Table II.

B. Temperature Shifts

The changes in line position, observed in going from one source temperature to another, are attributed to a
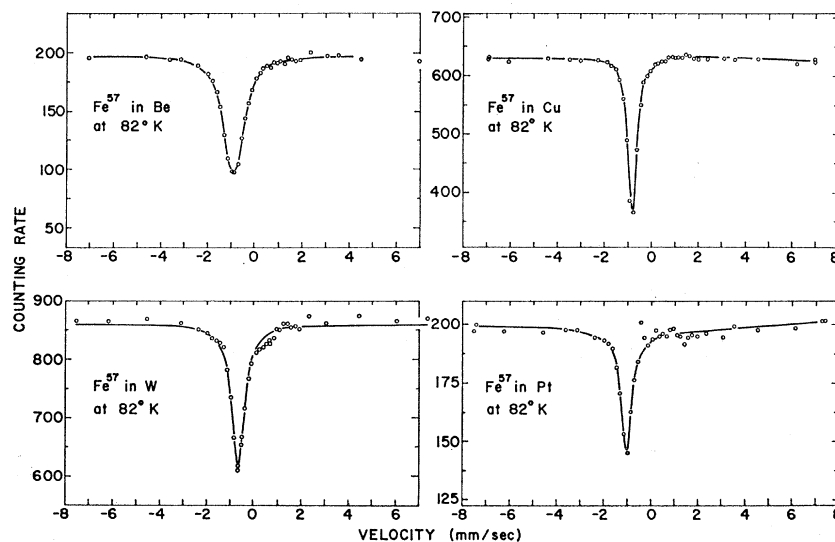

FIG. 1. Typical spectra for various sources. The absorber is enriched metallic Fe^{57} at 780°C.

[12] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128, 2207 (1962).

change in the mean-square velocity of the nuclei in the source and possibly to a temperature-dependent isomer shift.

The good agreement obtained[13] between experimental and theoretical values of the temperature coefficient of the Mössbauer resonance for metallic iron indicates that the temperature dependence of the isomer shift is less than 3×10^{-5} mm/sec per °K at room temperature. Since this effect is relatively small for pure iron, we assume that it is similarly small in the present cases and treat it as being zero. Thus we attribute our observed shifts entirely to changes in the mean-square velocity of the emitting nuclei.

Accordingly the mean-square velocity at 0°K is given[1,2] by

$$\langle v^2\rangle_0 = \langle v^2\rangle_T - 2c[S(T)-S(0)].$$

In order to apply this formula, we assume that at the

TABLE II. Parameters of absorption spectra as obtained by least-squares analysis. The error in $S(T)$ ranges from ±0.002 to ±0.006 mm/sec. The error in α ranges from ±0.002 to ±0.004. The error in β ranges from ±0.002 to ±0.016 mm/sec. In order to obtain shifts referred to the center of gravity of the six-line spectrum of metallic iron at 293°K, the quantity $+0.549$ mm/sec should be added to the values of $S(T)$ listed here.

Host material	Source temperature (°K)	$S(T)$ (mm/sec)	α	β (mm/sec)
Be	82	−0.891	0.509	1.010
	298	−0.781	0.465	0.979
	420	−0.695	0.441	0.963
Cu	82	−0.886	0.434	0.449
	298	−0.770	0.356	0.431
	420	−0.697	0.301	0.451
W	82	−0.669	0.281	0.66
	298	−0.553	0.296	0.61
	430	−0.455	0.258	0.59
Pt	82	−1.030	0.271	0.51
	298	−0.884	0.245	0.52
	425	−0.783	0.216	0.517

highest temperature T_3 of the source, the classical limit

$$\langle v^2\rangle_T = 3kT/m$$

is valid. It is to be noted that the classical limit is an expression of the equipartition theorem of statistical mechanics and is independent of the nature of the crystalline forces. Whether or not T is high enough for the limit to apply can be judged from the expansion of the Debye formula

$$\langle v^2\rangle_T = (3kT/m)[1+(1/20)(\Theta/T)^2$$
$$-(1/1680)(\Theta/T)^4+\cdots].$$

Furthermore, we assume that $S(0°K)=S(82°K)$, an approximation supported by the data[12] on metallic iron. Thus, the kinetic energy of an Fe⁵⁷ nucleus at 0°K has

[13] R. V. Pound, G. V. Benedek, and R. Drever, Phys. Rev. Letters **7**, 405 (1961).

TABLE III. Average kinetic energies of Fe⁵⁷ nuclei in various metals at 0°K. In the Debye theory, the zero-point kinetic energy is $(9/16)k\Theta$. $T_1=82$°K.

Host	T_3 (°K)	$S(T_3)-S(T_1)$ (cm/sec)	$\frac{1}{2}m\langle v^2\rangle_0$ from shift (eV)	Θ_s (°K)	$(9/16)k\Theta_s$ (eV)
Be	420	0.0195	0.0197	460	0.0223
Fe	370	0.0157	0.0201	400	0.0194
	718	0.0397	0.0226		
Cu	420	0.0189	0.0209	460	0.0223
W	430	0.0214	0.0177	400	0.0194
Pt	425	0.0246	0.0114	160	0.0078

been computed from

$$\tfrac{1}{2}m\langle v^2\rangle_0 = \tfrac{3}{2}kT_3 - mc[S(T_3)-S(T_1)].$$

The results of this computation are given in Table III. For comparison, values of the zero-point kinetic energy have also been computed from the effective Debye temperature Θ_s (see below).

Next we proceed to assign an effective Debye temperature Θ_s to each source. Each set of three shift measurements has been fitted to the equation

$$S(T)=S_0+\frac{9kT}{2mc}\left(\frac{T}{\Theta_s}\right)^3\int_0^{\Theta_s/T}\frac{x^3}{e^x-1}dx \qquad (2)$$

by adjusting the parameters S_0 and Θ_s to obtain a minimum in the sum of the squares of the deviations. Figure 2 shows the experimental values of the shift $S(T)$ and curves derived from Eq. (2).

In thus applying the Debye theory, one should convert experimental data (which are obtained at constant pressure) to the condition of constant volume.[13] In order to make such a correction, one needs to know the pressure shift, which has not yet been measured for the present cases. If this correction is of the same order of magnitude as in pure iron, then it can be neglected for our present purposes.
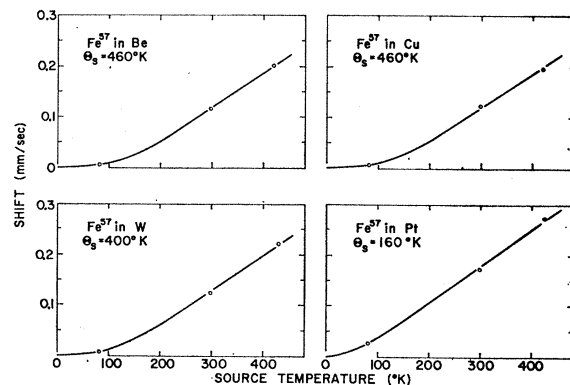

FIG. 2. Measured temperature shifts. The solid lines represent thermal shifts computed for the indicated values of Θ_s.

TABLE IV. Ratios of Mössbauer fractions and changes in the mean-square displacements of the radiating nuclei.

Host	f_2/f_1	f_3/f_1	$\langle r^2 \rangle_2 - \langle r^2 \rangle_1$ (Å²)	$\langle r^2 \rangle_3 - \langle r^2 \rangle_1$ (Å²)
Be	0.885	0.825	0.0069	0.0109
Cu	0.785	0.696	0.0137	0.0205
W	0.960	0.820	0.0023	0.0112
Pt	0.924	0.813	0.0045	0.0117
	error ≈ ±0.003		error ≈ ±0.0003	

C. Absorption Measurements

The recoilless fraction for an isotropic crystal lattice with harmonic forces is given by

$$f = \exp\left[-(4\pi^2/3)(E_\gamma/hc)^2 \langle r^2 \rangle_T \right].$$

For various reasons (in particular, because of uncertainty in subtracting the background) it is difficult to derive absolute values of f for the source from these data. However, since the area above the transmission dip is proportional to f, it is possible to obtain accurate values for the ratio of f at two different temperatures. A good measure of the area is the product of the fractional depth α and the width β, so that

$$f_2/f_1 = \alpha_2\beta_2/\alpha_1\beta_1.$$

It is noted that this relation is independent of a possible change in either the linewidth of the source or in any instrumental broadening in going from temperature 1 to temperature 2.

Such ratios are listed in Table IV, which also gives the differences in mean-square displacement calculated according to

$$\langle r^2 \rangle_2 - \langle r^2 \rangle_1 = 3/(4\pi^2)(hc/E_\gamma)^2 \ln(f_1/f_2).$$

Finally a Debye temperature Θ_f is obtained by fitting our data to the Debye-Waller expression

$$K\alpha\beta = f = \exp\left\{ \frac{-3E_\gamma^2}{mc^2 k\Theta_f}\left[\frac{1}{4} + \left(\frac{T}{\Theta_f}\right)^2 \int_0^{\Theta_f/T} \frac{x}{e^x - 1}dx\right]\right\}, \quad (3)$$

where K is a proportionality constant adjusted to give the best fit. Figure 3 shows the experimental values of

TABLE V. Comparison of Debye temperatures. The values of Θ_s and Θ_f for Fe⁵⁷ in iron were taken from Ref. 12. The values of Θ_{eff} have been computed according to Eq. (1) from values of Θ_{host} taken from the compilation by Holm.[a] The range of values of Θ_{eff} for each host reflects the range of values of Θ_{host} listed by Holm.

Host material	Θ_{eff} (°K)	Θ_s (°K)	Θ_f (°K)
Be	370−460	460±20	445±15
Fe	420−465	400±30	300−400
Cu	325−365	460±30	330±15
W	560−690	400±30	465±40
Pt	420−430	160±40	455±30

[a] M. W. Holm, Atomic Energy Commission Research and Development Report IDO-16399, 1957 (unpublished).

$\alpha\beta$, each multiplied by the appropriate value of K, and a curve plotted according to Eq. (3).

IV. DISCUSSION

In Table V we have collected the values of Θ_s and Θ_f resulting from our measurements. In order to facilitate comparison of these results with the simple expectation of Eq. (1), we have listed the appropriate values of Θ_{eff}. It is apparent that, with the exception of Θ_s for Pt, the simple expectation of Eq. (1) is in qualitative agreement with the experimental results. It is also clear that in the cases of Be, W, and Pt, the values of Θ_s and Θ_f are distinctly different from the Debye temperatures of the hosts. No simple theoretical explanation suggests itself for the anomalous value of Θ_s for Pt.

Our value of Θ_s for Be is in good agreement with that (480°K±100°K) of Maradudin et al.[5] Kistner and Mozer[14] report that Be containing Fe⁵⁷ in solid solution
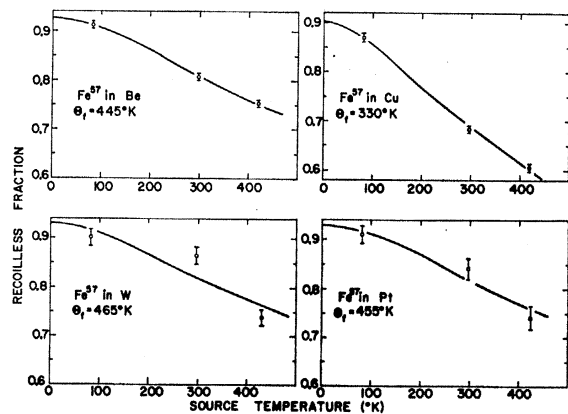

FIG. 3. Recoilless fractions. The experimental points are derived from measured relative values by multiplying with a constant so as to give a best fit to the Debye-Waller formula (solid curve).

exhibits a chemical shift of -0.11 ± 0.01 mm/sec with respect to a source of Co⁵⁷ in Cu, whereas specimens that were aged at 600°C exhibit a chemical shift of $+0.05 \pm0.01$ mm/sec. They suggest that the aging precipitates the iron in an (unknown) compound, and that the chemical shift of $+0.05$ mm/sec is characteristic of that compound. At 298°K our data give a chemical shift of -0.011 ± 0.004 mm/sec relative to Cu. This would indicate that our sample does not represent Fe⁵⁷ in solid solution in Be, nor does it correspond to the precipitated compound studied by Kistner and Mozer.

Since in the present work the resonant nuclei are in the form of Co during the heat treatment, the compounds they enter are not necessarily the same as those formed by an Fe impurity. Furthermore, the concentration of Co is lower by several orders of magnitude than the concentration of Fe in the absorber of Kistner

[14] O. C. Kistner and B. Mozer, Bull. Am. Phys. Soc. 7, 505 (1962).

and Mozer. Therefore different results may be produced by annealing. In any case, we are only in a position to note the agreement between our results for Θ_s and that of Maradudin et al.[5] and conclude that Θ_s does not seem to depend on the details of sample preparation. We are in no position to make any detailed assumptions concerning the condition of the Co^{57} in the Be lattice.

Our value of Θ_f for Cu is in reasonably good agreement with that $(360°K)$ of Dyson.[15] It is to be noted that Dyson prepared his source by melting the copper, whereas ours was obtained by diffusion.

[15] N. A. Dyson, Phys. Letters 1, 275 (1962).

Dipole-Narrowed Inhomogeneously Broadened Lines in Ferromagnetic Thin Films*

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An inhomogeneity in the magnetization of thin ferromagnetic films is shown to provide a mechanism for two-magnon scattering which contributes to the spin-wave resonance linewidth of thin ferromagnetic metal films. A normal (perpendicular) variation in the internal field has previously been assumed to explain the spinwave-resonance properties of thin films. In this work a planar variation in the magnetization is assumed which produces an inhomogeneously broadened linewidth. Since the inhomogeneity is much smaller than the average magnetization of the material, dipole forces will decrease the inhomogeneous broadening of the resonance line. Experimental results are in good agreement with the theory when eddy current losses are included and the inhomogeneity in the plane of the film is of the same order of magnitude as the normal inhomogeneity. As the film normal is rotated with respect to the magnetic field direction, the critical angle is approached at which the resonance conditions are the same throughout the film and the spins precess at a common frequency. At this angle the planar inhomogeneity will not be effective in broadening the excited mode. This effect is indicated in the data by a minimum in the frequency linewidth at this angle.

I. INTRODUCTION

THE inhomogeneous magnetization model[1,2] has been successful in accounting for many properties of thin-film spin-wave resonances.[3,4] It is assumed in this model that the inhomogeneity produces an internal field that is a maximum at the central plane of the film and decreases in a near parabolic manner to each surface (normal inhomogeneity). From an analysis of the data the total change in the internal field between the central plane and the film surface is $4\pi\Delta M \simeq 10^3$ G (Ref. 2). It is unlikely that this normal inhomogeneity will have the same properties everywhere in the plane of the film, i.e., there may be an inhomogeneity in the plane of the film (planar inhomogeneity). While the normal inhomogeneity will determine the position of the modes, the planar inhomogeneity will contribute to the line-width of the resonance modes.

In this paper, the planar inhomogeneity is assumed to be a dipolar disorder which produces a dipole-narrowed inhomogeneously broadened line. The line-widths predicted by this two-magnon scattering process

will be compared with the linewidths obtained from a 2.8×10^3 Å 80–20 Permalloy film at 9.6 and 14.6 kMc/sec.

The effect of inhomogeneities in the exchange field through a pseudodipolar interaction has been considered in detail by Clogston et al.[5] for ferromagnetic insulators. These field inhomogeneities arise from the disorder in the magnetic lattice through the random distribution of metal ions in the octahedral sites of the inverted spinel-structure ferrites and have a spatial periodicity comparable to the distance between spins. For this case the exchange field is the effective agent in narrowing the resonance line.

Geschwind and Clogston[6] have extended this mechanism to a disorder in the ordinary dipole interaction of polycrystalline ferromagnetic insulators, and find that under certain circumstances the dipole forces can reduce the inhomogeneous broadening of the magnetic resonance line. Here, as in thin ferromagnetic films, the inhomogeneity in the internal field is of such a spatial variation that the short-range exchange force coupling cannot tie together the motion of the spins. However, the long-range forces of the ordinary dipole interaction will become an effective agent in narrowing the res-

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[5] A. M. Clogston, H. Suhl, L. R. Walker, and P. W. Anderson, Phys. Chem. Solids 1, 129 (1956).

[6] S. Geschwind and A. M. Clogston, Phys. Rev. 108, 49 (1957).