Correlation between Mössbauer Resonance Strength and Second-Order Doppler Shift: Estimate of Zero-Point Velocity*

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Mössbauer results on the absolute resonance strength $\ln f$ and on the second-order Doppler shift are found to be approximately linearly related to each other for a variety of systems. This parametric representation of the experimental results (with temperature as a parameter) permits the deduction of the zero-point mean-square velocity of the resonant impurity nuclei. Data from a number of sources are presented, and various derived quantities are tabulated. The correlation is shown also to hold for two highly anharmonic cases. An experimental test of the Kagan relation between $\ln f$ at $T=0$ and the shift is given.

I. INTRODUCTION

AMONG the quantities which emerge from experimental Mössbauer effect (ME) studies are values for the temperature dependence of the recoil free probability f and the second-order Doppler shift $(\delta v/c)$. These quantities have been compared with various theoretical lattice models,[1,2] thus permitting estimates of anharmonicity and other effects.[3–6]

An approach not hitherto reported, and which we present here, is the parametric representation of the f factors and shifts. The utility of the method lies in its interrelation of two resonantly determined quantities, with no necessary recourse to externally measured parameters. The approach permits the direct determination of a parameter characterizing the density of states of the resonant impurity in its environment, and an estimate of the zero-point rms *velocity* of the resonant nuclei (the f factor at zero temperature yields a measure of the zero-point rms *displacement*).[7]

We restrict our attention to isotropic systems and assume localized modes to be sufficiently broad that they play a negligible role. In the harmonic approximation f_T (the recoil-free fraction at temperature T) and $\delta v/c$ (the second-order Doppler shift at temperature T) are given by

$$f_T=\exp(-\langle x^2\rangle_{\rm av}/\lambda\!\!\!^{-2}) \tag{1}$$

and

$$(\delta v/c)=-\langle v^2\rangle_{\rm av}/2c^2. \tag{2}$$

Here $\langle x^2\rangle_{\rm av}$ is the mean-square nuclear displacement of the emitting nucleus along the line of γ-ray emission, $\langle v^2\rangle_{\rm av}$ is its mean square velocity, δv is the Doppler velocity necessary to accomplish resonance, c is the velocity of light, and $\lambda\!\!\!^{-}=\hbar c/E$ is the reduced wavelength of the γ radiation having energy E. The ME nucleus may or may not be present as an impurity.

We have found that in a wide variety of situations a plot of $\ln f$ versus shift yields approximately a straight line. From this result we are able to deduce the zero-point velocity of the impurity nucleus, a quantity not accessible to other types of investigation.

In order to discuss this type of plot, and the results obtained therefrom, we summarize the predictions of the harmonic approximation for isotropic systems. We then specalize to the Debye model. Finally we present experimental data for a number of systems involving ^{57}Fe as a resonant impurity in a variety of host lattices, and ^{119}Sn in two compounds.

II. HARMONIC APPROXIMATION

In the harmonic approximation the mean-square displacement of an atom of mass m in an isotropic lattice is

$$\langle x^2\rangle_{\rm av}=(\hbar/m)\langle\omega^{-1}\rangle. \tag{3}$$

The mean-square velocity of an atom is

$$\langle v_x{}^2\rangle_{\rm av}=(\hbar/m)\,\langle\omega\rangle\,,\ \langle v^2\rangle_{\rm av}=3\langle v_x{}^2\rangle_{\rm av}=3(\hbar/m)\,\langle\omega\rangle\,, \tag{4}$$

where the expectation refers to a thermal average over

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[1] W. M. Visscher, Phys. Rev. **129**, 28 (1963); A. A. Maradudin and P. A. Flinn, *ibid.* **126**, 2059 (1962); K. N. Pathak and B. Deo, Physica **35**, 167 (1967).

[2] R. M. Housley and F. Hess, Phys. Rev. **146**, 517 (1966).

[3] W. A. Steyert and R. D. Taylor, Phys. Rev. **134**, A716 (1964).

[4] R. M. Housley, J. G. Dash, and R. H. Nussbaum, Phys. Rev. **136**, A464 (1964).

[5] R. M. Housley and F. Hess, Phys. Rev. **164**, 340 (1967).

[6] R. H. Nussbaum, D. G. Howard, W. L. Nees, and C. F. Steen Phys. Rev. **173**, 653 (1968).

[7] A. J. Boyle and H. E. Hall [Rept. Progr. Phys. **25**, 441 (1962)] note that an estimate of the zero-point velocity can be obtained from measurements of the temperature dependence of the shift alone. In their approach one must either assume a model or consider only the lowest temperature and highest temperature (classical region) data. Recently, M. G. Clark, G. M. Bancroft, and A. J. Stone [J. Chem. Phys. **47**, 4250 (1967)] have listed zero-point velocities determined for Fe in $BaFeSi_4O_{10}$ from ME measurements over the range 80–650°K assuming an Einstein model.

the impurity density of states;

$$\langle\omega^l\rangle=\int_0^\infty g(\omega)(\bar{n}+\tfrac{1}{2})\omega^l\,d\omega, \tag{5}$$

and the occupation number is $\bar{n}=1/(\exp(\hbar\omega/kT)-1)$. The density of states $g(\omega)$ is taken normalized to N degrees of freedom.

In case the impurity atom has a mass significantly different from the host atom, localized modes become important, and the formalism of the type developed by Visscher[1] or by Elliott[8] may be expected to modify this simplistic picture. However, Visscher has shown that in many circumstances a good first approximation is to use the Debye model, for which $g(\omega)\sim\omega^2$, and to use an effective Debye temperature given by $\Theta_D(m_h/m)^{1/2}$, where m_h is the host mass and m is the mass of the Mössbauer nucleus.

To discuss various models it is convenient to refer to the ratio of the logarithm of the recoil-free fraction to the shift associated with, say, a source. We define this ratio S_T by

$$S_T=\ln f_T/(\delta v/c). \tag{6}$$

The shift $\delta v/c$ will be related to the experimentally observed shift $\Delta E/E$ in Sec. III.

The ratio S_T can be evaluated for various models. On the Debye model one finds for temperatures $T\gtrsim 0.3\Theta_D$ that S_T is approximately constant, while for lower temperatures S_T decreases by a factor up to $\frac{2}{3}$, i.e., $S_{T\sim 0}\geq\frac{2}{3}S_T$. We have also evaluated S_T using the known phonon spectrum of metallic Fe.[9] A computed parametric plot of $\ln f_T$ versus $(\Delta E/E)_T$ for T up to 600°K is shown in Fig. 1. The low-temperature limiting slope for the true phonon spectrum is 0.699 times the high-temperature slope rather than the exact value $\frac{2}{3}$ of the Debye model. The high-frequency cutoff of the observed spectrum[9] is 450°K; the calculation of Fig. 1 is reproduced with precision using a Debye model with a characteristic temperature 413°K.

On an Einstein model the expectation values [Eqs. (3) and (4)] have the same temperature dependence, so that S_T is constant.

III. EXPERIMENTAL RESULTS

Our procedure has been to plot experimentally determined values of $\ln f_T$ against corresponding values of the shift $\Delta E/E$. The f values used are the *absolute* f values, and the observed Doppler shifts have been converted to relative γ-ray energy shifts to avoid the confusion of the sign of the Doppler velocity necessary to restore resonance when comparing both absorber and source experiments. It is to be emphasized that the shifts given in the following figures are the experimentally observed shifts. In this type of presentation temperature is a parameter and only quantities directly determined from ME experiments need be considered.

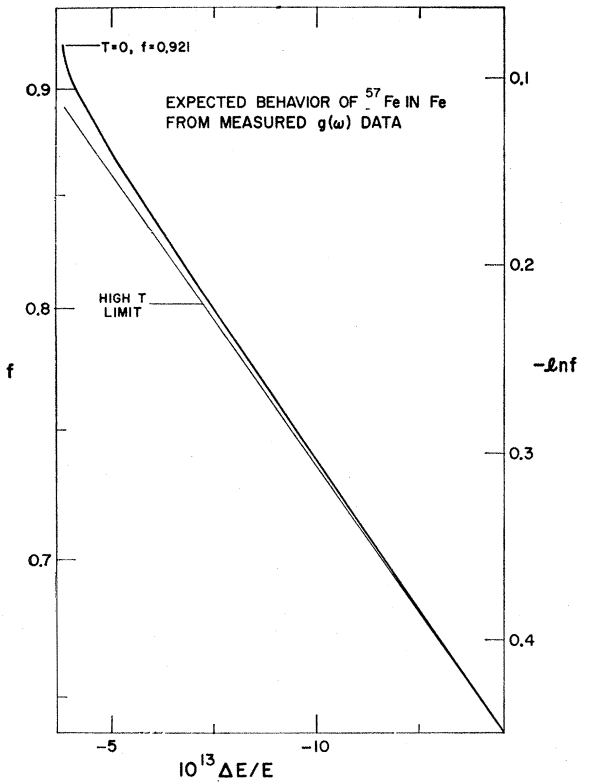

FIG. 1. Computed ME curve showing the recoil-free fraction f for the 14.4-keV γ rays from ^{57}Fe in Fe versus the fractional energy change of the γ ray due to second-order Doppler shift. The calculation shown represents the temperature range 0–590°K and utilized the room-temperature phonon-distribution function determined in Ref. 9.

In Fig. 2 we present such a curve for the 23.9 keV ME resonance in a SnTe absorber.[10] The source was ^{119m}Sn in SnTe held at 19.4°K; since neither f nor $\Delta E/E$ varies much with temperature below about 30°K, errors due to temperature drift in the source were minimized. A crude temperature scale for the data is given. The linearity of the plot is apparent except for the increase anticipated at the lowest temperatures. Thus we can refer to the slope S_T as a single dimensionless number characterizing a particular system at temperatures above some small fraction of the effective Debye temperature. From S_T and f_0 we show below that we can determine the absolute value of the mean-square zero-point velocity.

In Fig. 3 are similar data[11] for a Nb_3Sn absorber analyzed using a Pd_3Sn source at 19.4°K. The large isomer shift between source and absorber makes it difficult to obtain the shifts with high precision. The

[8] R. J. Elliott, in *Phonons in Perfect Lattices and Lattices with Point Imperfections*, edited by R. W. H. Stevenson (Oliver and Boyd, Edinburgh and London, 1967), Chap. 14.

[9] V. J. Minkiewicz, G. Shirane, and R. Nathans, Phys. Rev. 162, 528 (1967).

[10] R. D. Taylor and J. S. Shier (unpublished).

[11] J. S. Shier and R. D. Taylor, Phys. Rev. 174, 346 (1968).

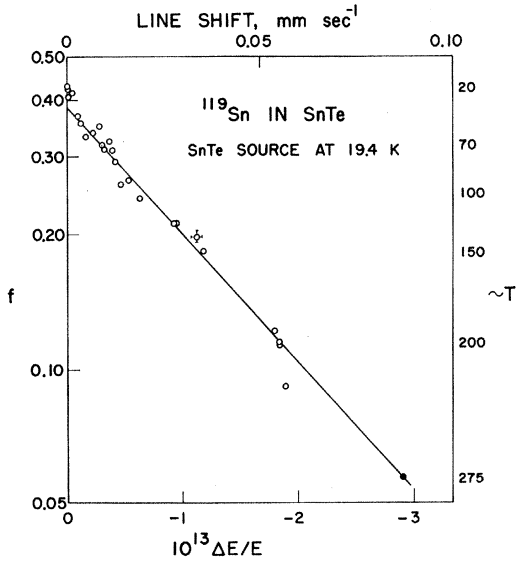

FIG. 2. Recoil-free fraction f versus γ-ray energy shift of the 23.9-keV γ ray of ^{119}Sn in a SnTe absorber. The Debye model (see also Fig. 1) predicts an upturn at low temperatures. The typical random error for these data (Ref. 10) is shown; the Doppler velocity necessary to restore resonance conditions is given at the top, and an approximate temperature scale is at the side.

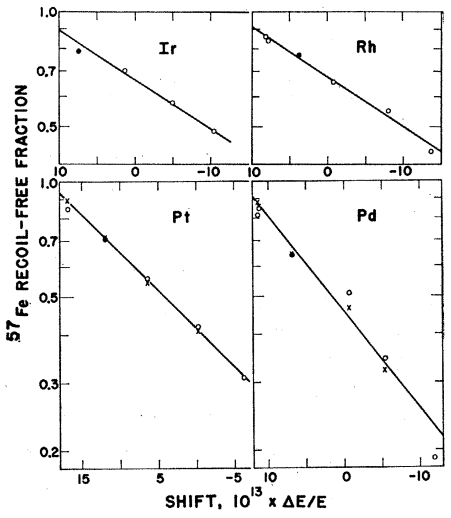

FIG. 4. Plots of $\ln f$ versus the observed γ-ray energy shift $\Delta E/E$ taken from ME studies (Ref. 3) of dilute ^{57}Fe in various hosts (circles). New measurements (Ref. 6) of f corresponding to the old shift (temperature) measurements are indicated by x's. The temperature range covered (Ref. 3) generally was 4–1020°K; the room-temperature data are shown as solid circles. Shift measurements are relative to an Fe absorber at 298°K. The straight lines determine the S_T values given in Table I.

scatter above 100°K is indicative of the precision. At lower temperatures a slight lattice phase change may complicate matters. Temperatures for four points are shown. The linearity over most of the temperature range is more striking when compared with the plots[11] of $\ln f$ versus T and $\Delta E/E$ versus T, neither of which has reached the limiting slopes at 300°K. Furthermore, a very high degree of anharmonicity for Nb_3Sn and SnTe is suggested[10–12] by the low values of f_0 combined with the very weak temperature dependence of f.

In Figs. 4 and 5 are the data obtained by Steyert and Taylor[3] for dilute ^{57}Fe in several cubic metallic hosts. The f values for these sources were determined using an enriched FeTi broad absorber at room temperature and the shifts using an Fe absorber. Temperatures ranged from 4 to 1020°K. On all graphs room temperature is indicated by the solid symbol. High-precision measurements of f_T for ^{57}Fe in Pt, Pd, and Cu have been recently reported[6] and are shown as x's for the temperatures common to both studies. It has been

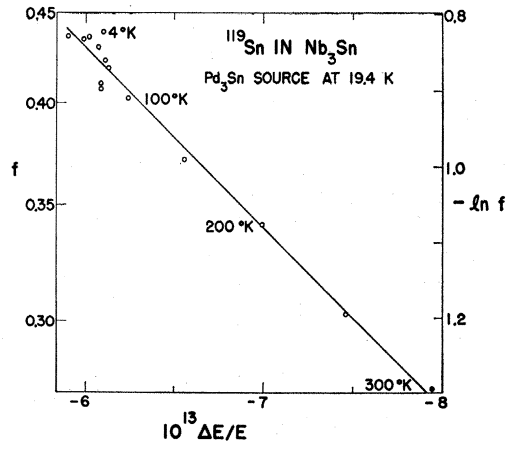

FIG. 3. The recoil-free fraction f versus the energy-shift data (Ref. 11) for the ^{119}Sn ME in a Nb_3Sn absorber. A few sample temperatures are indicated. Linearity even to the low-temperature region is in evidence despite the fact substantial anharmonicity is present (Refs. 11 and 12) as well as a small lattice-phase change.

[12] J. S. Shier and R. D. Taylor, Solid State Commun. 5, 147 (1967).

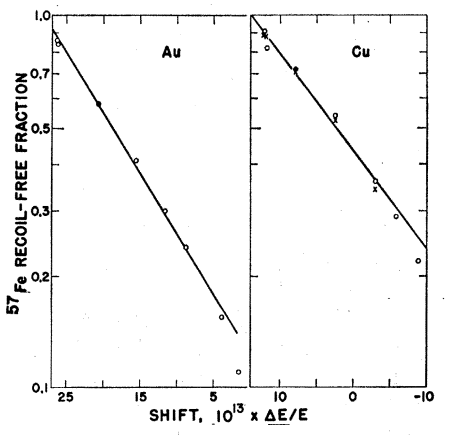

FIG. 5. Plots of $\ln f$ versus the observed γ-ray energy shift $\Delta E/E$ taken from ME studies (Ref. 3) of dilute ^{57}Fe in various hosts (circles). New measurements (Ref. 6) of f corresponding to the old shift (temperature measurements) are indicated by x's. The temperature range covered (Ref. 3). generally was 4–1020°K; the room-temperature data are shown as solid circles. Shift measurements are relative to an Fe absorber at 298°K. The straight lines determine the S_T values given in Table I.

suggested that apparent low f values at low temperatures may result from spontaneous magnetic ordering at a few of the Fe sites. For Pt, Pd, Au, and Cu this may account for the lack of a decrease of S_T at the lowest temperatures. Fe in Ir and Rh is almost nonmagnetic.

The determination of S_T requires only a knowledge of the relative f values with temperature; however, the absolute value of f at $T=0$ is needed in the analysis given in Sec. IV.

In the treatment of the data it is assumed that the only important temperature-dependent contribution to the shift is the second-order Doppler shift. Shifts due to source and absorber being unlike or the analyzing absorber not always being at the same fixed temperature from case to case do not affect the interpretation which follows. Other possible dependences of the shift on temperature, such as a variation of $|\psi(0)|^2$, the electron density at the site of the resonant nucleus, due to a change in pressure or volume, a phase change, or a temperature dependent isomer shift might slightly alter $S(T)$. Generally the high-temperature-shift data do approach the classical slope dictated by $\Delta E/E=-3kT/2mc^2$, suggesting that the assumption above is justified. Recently Housley and Hess[5] analyzed the shift data[3] taking into account the second-order Doppler shift and the volume expansion of the host in order to ascertain the presence of any temperature-dependent isomer shift. The results were inconclusive, so we must await better shift measurements.

IV. ANALYSIS OF THE DATA

In the graphs shown in Figs. 2–5 the shift (plotted as the abscissa) results from several terms:

$$\frac{\Delta E}{E}=\left[\left(\frac{\delta v}{c}\right)_T+\left(\frac{\delta v}{c}\right)_0\right]+\left(\frac{\delta v}{c}\right)_{\text{isomer}}+\left(\frac{\delta v}{c}\right)_{\text{abs}T}. \quad (7)$$

Here the first two terms taken together are the shift referred to in Eq. (2), which have now been separated into a temperature-dependent term and a zero-point term, so that

$$\frac{\delta v}{c}=\left(\frac{\delta v}{c}\right)_T+\left(\frac{\delta v}{c}\right)_0=-\frac{3kT}{2mc^2} \text{ for } T\gtrsim 2\Theta_D. \quad (8)$$

The third term arises from isomer shifts between the source and absorber if their compositions are not identical (and they never are in impurity studies), and the fourth term arises from the analyzing absorber being at a finite (but constant) temperature.

Using Eq. (6), we may rewrite Eq. (7) as

$$\ln f=S_T\left\{\frac{\Delta E}{E}-\left[\left(\frac{\delta v}{c}\right)_{\text{isomer}}+\left(\frac{\delta v}{c}\right)_{\text{abs}T}\right]\right\}. \quad (9)$$

Since the terms in square brackets are constant, S_T can be directly determined from experiment even though an arbitrary absorber is utilized.

If we can determine the slope S_0 at $T=0°$K, and since the recoil strength f_0 at $T=0°$K has been measured, we can determine the zero-point shift as

$$(\delta v/c)_0=(\ln f_0)/S_0. \quad (10)$$

On the Einstein model, $S_T=S_0$. For both the Debye model and for the actual phonon spectrum of metallic Fe we find that $S_0\sim\frac{2}{3}S_T$. Since existing experimental data at low temperature are not precise enough to determine S_0 directly, we will adopt $S_0=\frac{2}{3}S_T$ throughout this paper. Cases can be found (e.g., square well) in which S_T becomes arbitrarily small.[2] Only in the case of SnTe is the expected turn-up at low temperatures clearly observed in the data. The magnitude of the change supports the $\frac{2}{3}$ coefficient even though SnTe is known to be highly anharmonic. For the real case of a heavy impurity in a light lattice resulting in low-lying localized modes marked deviations from the $\frac{2}{3}$ value might be expected; no such data are available.

The experimental values of S_T determined from the straight-line fits shown in Figs. 2–5 (and for Ti) are given in Table I. The uncertainty in S_T is believed to be less than 10%. Values of f_0 given are minor extrapolations of $-\ln f$-versus-T curves of the various authors. Although for each case the uncertainty in f_0 is likely less than a few percent, most of the derived quantities described below are sensitive to its choice.

The values listed for Θ_D in row 1 of Table I were obtained from specific-heat measurements emphasizing the low-temperature measurements. The Θ_D values corrected by the procedure mentioned earlier yield the effective Θ_D values given in row 2. Θ_D values for Ir, Rh, and Ti as low as 285, 350, and 280°K have been reported. The agreement between the effective Θ_D listed and the Θ_{f_0} values derived from the listed f_0 values by $\Theta_{f_0}=-3R/(2\ln f_0)$ is not very good. (kR is the γ-ray recoil energy; $R=E^2/2kmc^2$.) Note that a change in f_0 of 0.01 for, say, Fe in Cu changes Θ_{f_0} by more than 10%.

The parameter S_T can be related to a frequency using Eqs. (3) and (4), and from this a characteristic temperature φ can be derived:

$$\langle v^2\rangle_{\text{av}}/\langle x^2\rangle_{\text{av}}=3\langle\omega\rangle/\langle\omega^{-1}\rangle=(k\varphi/\hbar)^2, \quad (11)$$

which is normalized so that $\varphi=\Theta_D$ at high temperatures. The result,

$$\varphi=(E/k)(2/S_T)^{1/2}, \quad (12)$$

does not involve f_0 explicitly and is given in row 5 of Table I; the comparison with the effective Θ_D is somewhat improved. Similarly, the determination of Θ_f using f data from a wide temperature range[3,6] yielded more consistent characteristic temperatures. In the case of Nb_3Sn (and SnTe, too) the f_0 is unusually low due to a high degree of anharmonicity.[11,12] Θ_{f_0} calculated

TABLE I. Mössbauer shift and recoil-free fraction are compared by studying plots of shift versus $\ln f$ with temperature as a parameter. A number of derived quantities are presented, including several characteristic temperatures and estimates of the zero-point velocities. Definitions are found in the text.

Parameter[a]		^{119}Sn SnTe	^{119}Sn Nb_3Sn	^{57}Fe Ir	^{57}Fe Rh	^{57}Fe Pt	^{57}Fe Pd	^{57}Fe Au	^{57}Fe Cu	^{57}Fe Ti	b
1 Θ_D, host[c]	(K)	···	228	420	478	233	275	165	335	430	(413)
2 $\Theta_D(m_h/m_i)^{1/2}$	(K)	···	···	771	642	431	376	307	354	394	413
3 f_0		0.43	0.44	(0.92)	0.87	0.91	0.90	0.87	0.91	0.82	0.921
4 Θ_{f_0}	(K)	53	54	···	245	361	323	245	361	172	413
5 φ	(K)	154	254	439	431	351	312	273	305	271	413
6 $f_0(\varphi)$		0.75	0.84	0.93	0.92	0.91	0.90	0.88	0.89	0.88	0.921
7 $S_T\times10^{-11}$		65.0	23.9	2.9	3.0	4.5	5.7	7.5	6.0	7.6	3.28
8 $x_{zp}\times10^{8}$	(cm)	0.076	0.075	0.040	0.051	0.042	0.044	0.051	0.042	0.061	0.0393
9 $v_{zp}\times10^{-4}$	(cm sec^{-1})	1.8_7	3.0_4	2.7_8	3.5_3	2.3_8	2.2_3	2.2_4	2.0_6	2.6_5	2.60
10 zp		2.7	4.3	0.99	1.6	0.90	0.88	1.03	0.78	1.4	0.919
11 $-(\delta v/c)_0\times10^{13}$		2.0	5.1	4.3	6.9	3.5	3.3	2.8	2.6	3.9	3.76

[a] Definition equations are given in the text. All quantities except Θ_D are deduced from ME measurements.
[b] ^{57}Fe in Debye solid with $m_{host}=57$, $\Theta_D=413$°K.
[c] D. Bijl, in *Progress in Low Temperature Physics* edited by C. J. Gorter (North-Holland Publishing Co., Amsterdam, 1957), Vol. 2, Chap. XIII.; except Nb_3Sn, L. J. Vieland and A. W. Wicklund, Phys. Rev. 166, 424 (1968). The Θ_D values derived from low-temperature specific heats are perhaps 10% higher than the Θ values appropriate to ME measurements (Ref. 6).

from f_0 as if it were harmonic is about four times lower than Θ_D found from specific-heat measurements. The value of φ determined by Eq. (12) is in much better agreement with Θ_D. The values of f_0 given by $f_0(\varphi)=\exp(-3R/2\varphi)$ are found in row 6.

The mean-square displacements are related directly to the absolute f values [Eq. (1)]. Hence at $T=0$ the zero-point displacement is

$$x_{zp}=\langle x_0^2\rangle_{av}^{1/2}=\lambda\!\!\!^{-}(-\ln f_0)^{1/2}=(\hbar c/E)(-\ln f_0)^{1/2}. \quad (13)$$

Values of x_{zp} using the f_0 values in row 3 are listed in row 8 of Table I.

Using Eqs. (2), (8), and (10), the rms velocity at $T=0$ is

$$v_{zp}=\langle v_0^2\rangle_{av}^{1/2}=c\left(\frac{-2\ln f_0}{S_0}\right)^{1/2}=c\left(\frac{-3\ln f_0}{S_T}\right)^{1/2}. \quad (14)$$

A tabulation of v_{zp} is given in row 9 of the Table I.

We have defined a dimensionless zero-point "uncertainty" parameter in terms of these quantities:

$$\text{zp}=(x_{zp})(m\,v_{zp})/\hbar. \quad (15)$$

On the Debye model $(\text{zp})_D=(27/32)^{1/2}=0.9186$; on the Einstein model $(\text{zp})_E=\sqrt{\frac{3}{4}}=0.866$; for a square well $(\text{zp})_{SW}=(\frac{1}{2}\pi^2-3)^{1/2}=1.391$. For the Fe impurity cases where anharmonicity is believed to be minor, there is consistency to within the limits expected by the uncertainty in f_0 and S_T. The derived zero-point quantities for the two ^{119}Sn cases are probably not meaningful in view of the large anharmonicity; nevertheless, the consistancy of S_T over a wide range of T is reemphasized.

In row 11 of Table I is listed the zero-point Doppler shift for sources to facilitate comparison of magnitudes of the shift with the figures. Also, column b gives the parameters derived for a ^{57}Fe Debye solid with $\Theta_D=413$°K.

V. KAGAN'S RESULT

A method of analysis supplemental to that preceding has been proposed by Kagan.[13] He finds that for a harmonic system the temperature-dependent part of the second-order Doppler shift is related to the zero-temperature recoil-free fraction, viz.,

$$-\ln f_0=\frac{2}{\pi^2}\frac{E^2}{k^2}\int_0^\infty\left[\left(\frac{\Delta E}{E}\right)_T-\left(\frac{\Delta E}{E}\right)_{T=0}\right]\frac{dT}{T^3}. \quad (16)$$

The term $(\Delta E/E)_{T=0}$ is the experimental value of the shift at $T=0$, and $(\Delta E/E)_T$ is the observed shift. To be more precise, $(\Delta E/E)_T$ is the second-order Doppler-shift contribution to the observed shift. As in preceding sections we take other temperature-dependent contributions to be small or self-compensating.

We have evaluated this integral for several systems. The results are summarized in Table II. The low-temperature contribution to the integral in Eq. (16) is critically dependent on the choice of $(\Delta E/E)_{T=0}$ and the shape of the curve through the data. Even the most precise data available are inadequate below about 20°K. Therefore we have chosen $(\Delta E/E)_0$ to be that which gives the best fit at low T to $(\Delta E/E)_T=AT^4$, the functional form given by the Debye model near $T=0$. At high temperatures the shift must approach $\Delta E/E=-3NkT/2mc^2$. A smooth splined curve was drawn through the data in the intermediate range. Numerical integration of the intermediate region plus the analytical extension at the temperature extremes resulted in the f_0 values given in Table I. The relative contributions of the low- and high-temperature integrals were about 10 and 20%, respectively, so that most of the contribution to Eq. (16) is indeed governed by the data. Only three of the seven ^{57}Fe systems studied[3] are

[13] Yu. Kagan, Zh. Eksperim. i Teor. Fiz. 47, 366 (1964) [English transl.: Soviet Phys.—JETP 20, 243 (1965)]. The $-\ln f$ value predicted by his Eq. (3.8) is a factor of 2 too high. See also Ref. 2.

TABLE II. Kagan has proposed a relationship between a temperature integral of the Mössbauer second-order Doppler shift and the zero-temperature resonance strength. The table reports tests of this relationship for several cases. The f_0 column represents the result of performing Kagan's integral, and the f column presents the results of direct and extrapolated f measurements at low temperatures.

System	Shift measurements f_0, Eq. (16)	f measurements f	T (°K)
^{57}Fe in Cu	0.90_5[a]	0.910±0.002[b]	4
		(0.913)[c]	0
^{57}Fe in Pd	0.91_3[a]	0.891±0.002[c]	19
		0.875±0.002[c]	13
		(0.896)[c]	0
^{57}Fe in Pt	0.89_9[a]	0.905±0.003[c]	20
		0.897±0.003[c]	11.8
		(0.912)[c]	0
^{119}Sn in SnTe	0.79_4[d]	0.43 ±0.05[d]	19.4
^{119}Sn in Nb_3Sn	0.84_9[e]	0.44 ±0.05[e]	4

[a] Reference 3.
[b] D. L. Sprague, cited in Ref. 6.
[c] Reference 6.
[d] Reference 10.
[e] Reference 11.

listed; the recent detailed temperature studies of Nussbaum *et al.*[6] allow a ready comparison in these cases. The good agreement confirms the Kagan theory.

The application of Eq. (16) to SnTe and Nb_3Sn yield f_0 values much higher than are observed. In view of the large anharmonicity,[11,12] the Kagan theory should not be expected to apply. Curiously, the f values $[f_0(\varphi)]$ determined from the S_T values found in Table I are almost the same as those found here, even though they do not utilize the same data.

Dash, Johnson, and Visscher[14] have investigated the effects of anharmonicity on the f value. At high temperatures they show that the observed f may be represented by a product $f_h \cdot f_a$, where the subscripts refer to an harmonic term and an anharmonic term. Taking f_a to be temperature-independent, Shier and Taylor[11] were able to represent their f data; the harmonic term corresponded to a Θ_D of several hundred degrees, again in sharp contrast to that found from f_0 alone and in crude agreement with the φ value of Table I.

[14] J. G. Dash, D. P. Johnson, and W. M. Visscher, Phys. Rev. **168**, 1087 (1968).

VI. CONCLUSIONS

The analysis presented here permits the derivation of quantities related directly to the zero-point velocity of the impurity atoms in the case of ^{57}Fe in a variety of host lattices and of ^{119}Sn in two compounds. The high-temperature linear correlation of $\ln f$ versus shift is found to hold (to within the precision of the data) over a wide range of temperature, perhaps even lower than that suggested by the Debye model. This correlation applies even in the presence of large anharmonic contributions. Very precise measurements over a wide range of the shift and f value on systems likely to show harmonic behavior would allow a more stringent test of the assumption that $S_0=\frac{2}{3}S_T$.

An experimental test of the Kagan relation which yields f_0 from second-order Doppler-shift measurements was impressively good for the (almost) harmonic cases. A treatment of the behavior of the shift in the presence of anharmonicity is called for in order to interpret $T=0$ and zero-point parameters for the highly anharmonic systems included.

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