Analysis of Debye-Waller–Factor and Mössbauer-Thermal-Shift Measurements. II. Thermal-Shift Data on Fe

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Techniques developed in a previous paper are used to subtract the second-order Doppler contribution from measured thermal shifts on pure Fe and dilute Fe in various hosts. This allows the temperature dependence of the isomer shift arising from the electron density at the nucleus to be seen more clearly than was previously possible. It is shown that this temperature dependence cannot be accounted for by thermal expansion alone. In pure Fe a contribution related to the magnetization is clearly evident, as is theoretically expected. A contribution in addition to this and the thermal-expansion contribution is present, contrary to the conclusion generally drown from previous work. The additional contribution to the isomer shift is discussed in terms of two theories which have been used to explain the temperature dependence of hyperfine coupling constants.

1. INTRODUCTION

THE dominant term in the temperature shift of the Mössbauer resonance energy, at least in the case of Fe^{57}, is the second-order Doppler shift caused by the temperature dependence of the mean-square velocity of the emitting or absorbing nuclei. Because of this, little is known about the temperature dependence of the isomer shift caused by a change with temperature of the electron density at the nucleus. In a preceding paper,[1] we derived general formulas relating the mean-square velocity of a particular atom in an arbitrarily complicated solid to other measurable quantities. In this paper we use these results to separate the second-order Doppler shift from thermal-shift data on pure Fe and dilute alloys of Fe in several hosts.[2,3]

In general, we find that for temperatures above about the effective Debye temperature there is good evidence for a contribution to the isomer shift which corresponds to an *increase* in electron density at the nucleus with temperature. This is in addition to and sometimes larger than the nearly linear decrease in electron density caused by the volume expansion.[4–6]

The contribution corresponding to an increase in electron density can be qualitatively accounted for by two theories[7,8] which have been proposed to account for the temperature dependence of hyperfine coupling constants.[8–10]

In pure Fe we find a contribution to the isomer shift which appears to be proportional to the magnetization. This is to be expected from band-theory models of Fe as has been mentioned.[11,12] Our result is in agreement with the theoretical estimates of the effect.

2. ANALYSIS OF PURE-Fe DATA

The most extensive set of thermal-shift measurements which have been reported so far are those of Preston, Hanna, and Heberle[2] on pure Fe. Fortunately, accurate phonon-dispersion curves at room temperature in pure Fe have recently been measured by neutron-diffraction techniques.[13] Interatomic force constants derived from these neutron data can be used in Eq. I-12 to give the second moment of the frequency spectrum. The result is $\omega^2(2) = 1.831 \pm 0.023 \times 10^{27}$ sec^{-2}. This second moment would be given by a Debye spectrum with $\Theta = (422 \pm 3)°K$. The force constants in a five-neighbor model are over determined by the neutron data. Therefore, our estimated errors are realistic assuming only that the five-neighbor fit to the phonon-dispersion curves is adequate. {*Note added in proof.* Another set of atomic force constants determined from neutron diffraction data and low-frequency elastic constant measurements has recently been reported. [B. N. Brookhouse, H. E. Abou-Helal, and E. D. Hallman, Solid State Commun. 5, 211 (1967).] These give $\omega^2 = 1.770 \times 10^{27}$ sec^{-2} and $\theta = 415°K$. Using these values does not qualitatively affect our analysis.}

[1] R. M. Housley and F. Hess, Phys. Rev. 146, 517 (1966), hereafter referred to as I. We denote equations of this paper by I-1, I-2, etc.

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[7] E. Simanek and R. Ohrbach, Phys. Rev. 145, 191 (1966); E. Simanek and N. L. Huang, Phys. Rev. Letters 17, 699 (1966).

[8] G. B. Benedek and J. Armstrong, J. Appl. Phys. 32, 1065 (1961).

[9] W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. 139, A1338 (1965).

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[11] S. Alexander and D. Treves, Phys. Letters 20, 134 (1966).

[12] R. Ingalls, Phys. Rev. 155, 157 (1967).

[13] J. Bergsma, C. van Dijk, and D. Tocchetti, Phys. Letters 24A, 270 (1967).

TABLE I. Thermal-shift data for pure Fe.

(1) T °K	(2) $-\frac{1}{8}(1/mc^2)$ $\times[\hbar^2\omega^2(2)/kT]$	(3) $+1/480$ $(1/mc^2)[\hbar^4\omega^4(2)/k^3T^3]$	(4) $-(2)$ $\times\{1-[1+0.00029(T-300)]^{-1}\}$	(5) $(\Delta E/E)_{corr}$	(6) $M(T)/M(0)$
198.0	-1.094×10^{-13}	0.083×10^{-13}	0×10^{-13}	3.929×10^{-13}	0.988
293	-0.740	0.026	0	3.943	0.978
293.9[a]	-0.738	0.026	0	4.004	0.978
298	-0.727	0.025	0	4.028	0.974
370	-0.586	0.013	0.011	4.172	0.960
372.6[a]	-0.582	0.013	0.011	4.000	0.966
497.4[a]	-0.436		0.022	4.228	0.932
613.7[a]	-0.353		0.028	4.270	0.894
717.6	-0.304		0.031	4.348	0.841
718.0[a]	-0.304		0.031	4.358	0.844
816.0[a]	-0.266		0.032	4.135	0.776
912.3	-0.237		0.034	4.118	0.688
912.5[a]	-0.237		0.034	4.188	0.688
1019.0[a]	-0.213		0.035	4.119	0.393
1019.2	-0.213		0.035	4.059	0.387
1039.4	-0.208		0.035	4.145	
1040.3[a]	-0.208		0.035	4.234	
1042.1	-0.208		0.035	4.177	
1042.8	-0.208		0.035	3.960	
1043.4	-0.208		0.035	4.344	
1043.7[a]	-0.207		0.035	3.750	
1046.0[a]	-0.207		0.035	3.973	
1046.1	-0.207		0.035	3.906	
1048.1[a]	-0.207		0.035	3.822	
1054.6	-0.205		0.035	3.647	0
1084.6	-0.200		0.035	3.803	0
1104.7	-0.196		0.035	3.823	0
1124.3	-0.193		0.035	3.796	0
1144.7	-0.189		0.035	3.756	0
1164.8	-0.186		0.035	3.807	0
1184.9	-0.183		0.035	3.861	0

[a] Identifies data on the Fe sample which was not decarburized. Data near Curie temperature is between horizontal lines.

Knowing the second moment of the frequency spectrum, we can calculate the second-order Doppler shift for $T\gtrsim200°$K by use of Eq. I-17. The first term corresponding to the classical high-temperature limit is -2.4372×10^{-15} T. It should be emphasized that this limit follows from applying the equiposition theorem to the terms in the Hamiltonian corresponding to the *momenta* of the particles and is hence generally valid. In particular, it is correct for an anharmonic crystal. The second term with the $\omega^2(2)$ value listed above is $2.169\times10^{-11}/T$ and is given in column 2 of Table I. The value of the third term estimated by assuming $\omega(4)=\omega(2)$ is given in column 3. From comparison with other metals,[14] this latter assumption is thought to be correct to within about 10%. This contribution is seen to be negligible above room temperature.

It is known that the quasi-harmonic frequencies of a lattice generally decrease with increasing temperature. The temperature dependence of sound velocities in Fe has been measured.[15] From these data we can estimate that above about 300°K the slope of the second moment versus temperature will be about -5.3×10^{23} sec$^{-2}/°$K. The changes in shift caused by this estimated temperature dependence are listed in column 4 of Table I. In addition to this, there will be an explicit contribution to the shift due to anharmonic terms which are not accounted for by the quasi-harmonic shifts in lattice frequencies. No theoretical estimates of this contribution have been published. However, Maradudin and Flinn[16] did an analogous calculation for the mean-square displacement in an anharmonic model crystal. They found that the explicit contribution to the mean-square displacement was of the opposite sign and less than half as large as the one due to quasi-harmonic frequency shifts.

Column 5 of Table I gives the final isomer-shift values obtained from the data of Preston, Hanna, and Heberle after correcting for second-order Doppler effects. It is to be noted that the two terms which are somewhat uncertain are quite small. In fact, the correction for anharmonic effects could be neglected or doubled without affecting any of our conclusions. The over-all subtraction of the second-order Doppler shift is probably accurate to about 0.03×10^{-13}. The statistical uncertainty in the data is about 0.1×10^{-13}.

The results (column 5) for the temperature-dependent isomer shift are plotted in Fig. 1. It is immediately

[14] L. Salter, Advan. Phys. **14**, 1 (1965).
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[16] A. A. Maradudin and P. A. Flinn, Phys. Rev. **129**, 2529 (1963).
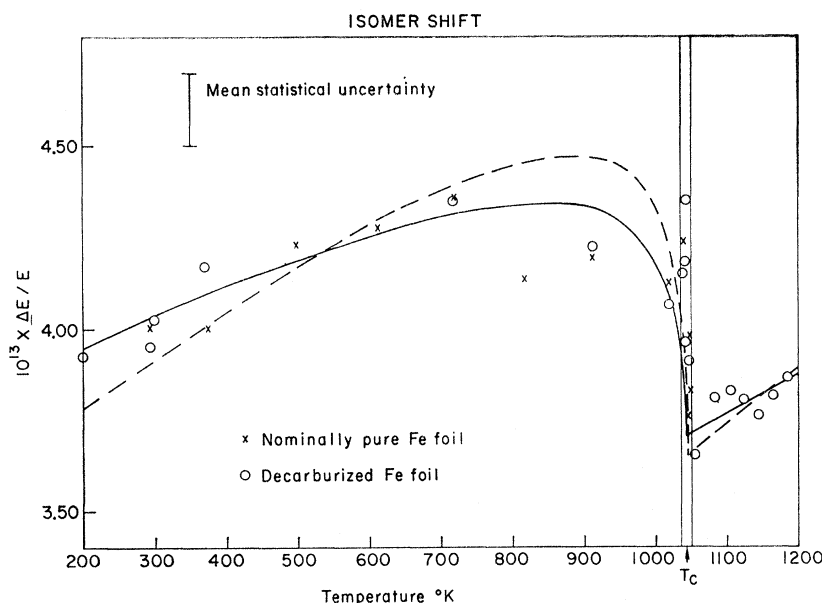
FIG. 1. Isomer shift of pure Fe versus temperature obtained by correcting the thermal-shift data of Preston, Hanna, and Heberle, (Ref. 2) for the second-order Doppler contribution.

noticed that the experimental points near the Curie temperature show considerable scatter. We assume this arises from difficulty in computer fitting the overlapping line spectra, and hence, we disregard the data in the temperature range between the two vertical lines. The remaining points suggest that there is a term in the shift approximately proportional to the magnetization and an additional term which is approximately linear with temperature. The anomaly in the thermal expansion of Fe due to the change in magnetization[17] is much too small and of the wrong character to account for the sharp change in isomer shift seen near the Curie temperature.

We have fit the Fe data using the two assumed functional forms

$$(\Delta E/E)_{corr}=A+sT+x[M(T)/M(0)] \quad (1)$$

and

$$(\Delta E/E)_{corr}=A+s_0T+rT^2+x[M(T)/M(0)], \quad (2)$$

where M is the magnetization, T the temperature, and s_0 the temperature slope that would be calculated from thermal expansion alone. The reason for choosing these forms is discussed in Sec. 4. The best fit to Eq. (1) corresponds to $s=1.0\pm0.3\times10^{-16}/°K$ and $x=1.1\pm 0.3\times10^{-13}$. This value of s is listed in Table III. The calculated curve using these parameters is shown by the solid line in Fig. 1. The dashed line shows an obviously poorer fit obtained with $s=1.6\times10^{-16}/°K$ and $x=1.5\times10^{-13}$. The best fit to Eq. (2) yields $r=-1.1\pm0.3\times10^{-19}/°K^2$ and $x=0.5\pm0.3\times10^{-13}$. This fit, although not shown in Fig. 1, is as good as the solid-line best fit obtained with Eq. (1).

3. ANALYSIS OF DILUTE Fe ALLOY DATA

Thermal shifts over a wide temperature range for dilute Fe in several host metals have been reported by

Steyert and Taylor.[3] In these cases values of the appropriate weighted second moments for use in Eq. I-17 are not available. However, from the f values reported, the corresponding weighted minus second moments can be determined by use of Eqs. I-18 and I-39. Since it was shown in I that the weighted second moment is greater than or equal to the inverse of the weighted minus second moment, this gives a lower limit for the value of the weighted second moment.
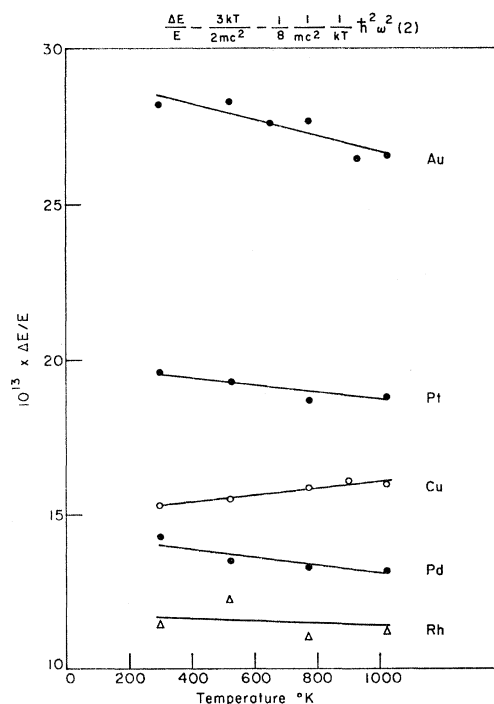

FIG. 2. Isomer shift of Fe in various hosts versus temperature from the data of Steyert and Taylor (Ref. 3).

[17] F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).

TABLE II. Raw and corrected $\Delta E/E \times 10^{13}$ for Fe in various hosts.

T °K	Au data	Au corr	Pt data	Pt corr	Cu data	Cu corr	Pd data	Pd corr	Rh data	Rh corr
298	20.8	28.2	12.0	19.6	7.8	15.3	6.8	14.3	3.8	11.4
523	15.5	28.3	6.4	19.3	2.6	15.5	0.6	13.5	−0.8	12.2
648	11.7	27.6	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯
773	8.8	27.7	−0.3	18.7	−3.0	15.9	−5.6	13.3	−8.0	11.0
898	⋯	⋯	⋯	⋯	−5.9	16.1	⋯	⋯	⋯	⋯
923	3.9	26.5	⋯	⋯	⋯	⋯	⋯	⋯	⋯	⋯
1023	1.6	26.6	−6.2	18.8	−9.0	16.0	−11.8	13.2	−13.8	11.2

Using these lower limits, one can partially correct the data for the second-order Doppler shift. The raw and corrected shifts are shown in Table II, and the corrected values are plotted in Fig. 2. Straight lines corresponding to visual best fits are drawn, and the slopes are listed in Table III. Use of the correct room-temperature second moments would give slopes which are more negative. Also, allowing the second moments to decrease with temperature would give more negative slopes. Therefore, except for the statistical uncertainty, linear fits to the isomer-shift data will have slopes at least as negative as those listed. Equally good fits can be obtained assuming

$$(\Delta E/E)_{\text{corr}} = A + s_0 T + rT^2.$$

4. DISCUSSION

The pressure and temperature dependence of the shift in pure Fe was discussed some time ago by Pound, Benedek, and Drever.[4] They concluded that the temperature dependence of the isomer shift could be adequately accounted for by thermal expansion alone. The shifts with volume for Fe and for Fe in all hosts under discussion except Rh have been determined from pressure-shift and compressibility measurements[5,6] and are listed in column 2, Table III. Average thermal-expansion coefficients for the temperature range of the shift measurements are listed in column 3. The product giving the calculated slope s_0 for the temperature dependence of the isomer shift, assuming it is due to thermal expansion alone given in column 4, can be compared with the observed slopes given in column 5. It is seen that the observed slopes are always consider-

ably smaller than calculated, even for pure Fe. This disagreement with the conclusions of Pound, Benedek, and Drever comes primarily from our use of a better method of correcting for the second-order Doppler shift. Their experimental results and the later ones we use agree excellently. Our method of correction using data determined from neutron-diffraction measurements is not influenced by magnetic contributions which affect the specific heat. Our calculated slope for the second-order Doppler shift at 297°K is $-2.19 \times 10^{-15}/°\text{K}$, which is to be compared with their $-2.28 \times 10^{-15}/°\text{K}$. Subtracting this new value from their measured slope leaves $0.10 \pm 0.05 \times 10^{-15}/°\text{K}$. Their calculated-slope difference (using the thermal-expansion coefficient at room temperature) is $0.15 \times 10^{-15}/°\text{K}$. The difference of $0.5 \pm 0.6 \times 10^{-16}/°\text{K}$ is quite consistent with our higher temperature result (see Table III) of $0.9 \pm 0.3 \times 10^{-16}/°\text{K}$.

The Mössbauer isomer shift depends on the total electron density at the nucleus, while the hyperfine coupling constant for Fe depends primarily on the spin-up minus the spin-down density. A close relationship between the temperature dependences of these two quantities is clearly to be expected. At least two theories have been proposed to account for the temperature dependence of hyperfine coupling constants.

In 1961, Benedek and Armstrong[8] demonstrated a significant temperature dependence of the hyperfine coupling constant in pure Fe. Following a suggestion by Kittel, they developed a theory in which the temperature dependence comes from the thermal excitation of d electrons to higher-energy states. On the basis of band-structure calculations, the radial wave functions of the d electrons were assumed to be strongly energy-

TABLE III. Comparison of calculated and measured slopes of isomer shift versus temperature for Fe in various hosts.

(1) Host	(2) $(d \ln E/d \ln V)$ [a]	(3) $(d \ln V/dT)$ [b]	(4) $(d \ln E/dT)_{\text{calc}}$	(5) $(d \ln E/dT)_{\text{exp}}$	(6) (4) − (5)
Fe	4.3×10^{-12}	$4.5 \times 10^{-5}/°\text{K}$	$1.9 \times 10^{-16}/°\text{K}$	$1.0 \times 10^{-16}/°\text{K}$	$0.9 \times 10^{-16}/°\text{K}$
Cu	2.0	5.6	1.1	1.0	0.1
Rh	⋯	⋯	⋯	−1.0	⋯
Pd	2.0	4.1	0.8	−1.4	2.2
Pt	1.3	3.1	0.4	−0.9	1.3
Au	1.3	4.7	0.6	−2.1	2.7

[a] Reference 6.
[b] W. E. Forsythe, Smithsonian Inst. Misc. Collections 120, 145 (1959); F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).

dependent. This theory gives a hyperfine coupling constant that varies quadratically with temperature. The predicted temperature dependence of the isomer shift would be the same.

More recently, Walsh, Jeener, and Bloembergen[9] have demonstrated an explicit dependence of the hyperfine coupling constant of Mn^{++} and V^{++} in MgO and Mn^{++} in several other cubic hosts on temperature. Since these materials are insulators, the theory of Benedek and Armstrong cannot apply. Simanek and Ohrbach, and Simanek and Huang[7] have proposed an explanation in which excited electronic states are mixed into the ground state by the orbit-lattice interaction. This gives a contribution to the hyperfine coupling constant and, correspondingly, to the electron density at the nucleus which varies as the mean-square amplitude of certain components of the local strain.

The temperature dependence of the mean-square local-strain components has certain characteristics in the harmonic approximation which may be derived in a manner analogous to that used for the discussion of mean-square displacements in I. For an arbitrary component of local strain in an arbitrarily complicated crystal, we may write

$$\langle (x_{jk}-x_{j'k'})^2 \rangle_T = \sum_i \left(\frac{b^2_{jki}}{m_k} + \frac{b^2_{j'k'i}}{m_{k'}} - \frac{2b_{jki}b_{j'k'i}}{(m_{k'}m_k)^{1/2}} \right)$$

$$\times \{\tfrac{1}{2}+[\exp(\hbar\omega_i/kT)-1]^{-1}\} (\hbar/\omega_i),$$

where the notation is defined in I. From this it is seen that the qualitative features of the temperature dependence are the same as those of the mean-square displacement. $\langle (x_{jl}-x_{j'k'})^2 \rangle_T$ is a monatonic increasing function with positive curvature. It has 0 slope at $T=0$ and approaches a constant slope at high temperature. It is *not*, in general, proportional to the lattice thermal energy as was the case for the model used by Simanek, Ohrbach, and Huang.[7] As with the mean-square displacement, the high-temperature slope of this quantity determines a *maximum* low-temperature intercept. However, since this relation is not linear, it cannot be carried over directly to the resulting changes in isomer shift and hyperfine coupling. In addition, there is no reason why the mean-square strain cannot continue nearly linearly to values much lower than this maximum. A case where this appears to happen has been observed[10] for Mn^{++} in SrO.

As Simanek and Ohrbach state, the first deviations from the low-temperature limiting value of the mean-square strain should go as T^4. However, as with the T^3 law for specific heat, the range of validity of this expression is expected to be very limited. Therefore, it is not surprising that no data obeying a T^4 relation have been reported.

We have assumed that the various contributions to the isomer shift including the one due to thermal expansion are additive. Since only small changes in

electron density are involved, this seems reasonable, although a rigorous justification cannot be given.

5. CONCLUSIONS

A temperature dependence of the isomer shift which cannot be accounted for in terms of thermal expansion alone has been demonstrated for pure Fe and dilute Fe in several alloys. In the case of pure Fe, this is contrary to the view which has been generally accepted since the work of Pound, Benedek, and Drever.[4]

A contribution to the shift proportional or nearly proportional to the magnetization has been demonstrated to exist in Fe. This has been predicted by Alexander and Treves[11] and by Ingalls.[12]

The analysis suggests that the temperature dependence of the hyperfine coupling constant for iron alloys and probably also for iron salts should be of the same order of magnitude as that observed in pure Fe. This is in agreement with magnetization-versus-temperature and internal-field–versus–temperature measurements on several ferrites. The data have been assembled by J. J. van Loef.[18]

The same effect can perhaps be observed in the paramagnetic Mössbauer hyperfine spectra seen for well-separated Fe^{+++} ions. A possible example can be seen in the temperature dependence of spectra reported by Wertheim and Remeika[19] for Fe in Al_2O_3. Spectra calculated by van der Woude[20] show that under the influence of a temperature-dependent paramagnetic relaxation time alone the outer lines should broaden and disappear before the splitting has decreased by more than about 5%. In the data the outer lines are still resolved with a 15% decrease in splitting at $T=498°K$. In ferrichrome A the outer lines disappear at $T=31°K$ with a negligible change in splitting.[20]

More precise thermal-shift data should make it possible to decide which, if either, of the mechanisms discussed above makes the major contribution to the explicit temperature dependence of the isomer shift in Fe and Fe alloys. About an order-of-magnitude greater accuracy is needed. This is possible with experimental techniques now available.

[18] F. van der Woude (private communication). Similar spectra for $S=\tfrac{1}{2}$ have been published. F. van der Woude and A. J. Dekker, Phys. Status Solidi **9**, 775 (1965).

[19] G. K. Wertheim and J. P. Remeika, in *Nuclear Magnetic Resonance and Relaxation in Solids*, edited by L. van Gerven (North-Holland Publishing Company, Amsterdam, 1965), p.157.

[20] H. H. Wickman, M. P. Klein, and D. A. Shirley, Phys. Rev. **152**, 345 (1966).