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Magnetization and Temperature Dependence of the Mössbauer Spectrum Shift for an Insulator*

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The results of a Mössbauer-effect study of $HoFeO_3$ in the temperature range 99–875°K are presented. Special attention is paid to the shift of the center of the spectrum and its temperature dependence both above and below the Néel point T_N. Although no discontinuity is found at the Néel temperature, the total shift has a different temperature dependence for $T<T_N$ and for $T>T_N$. The experimental results are compared with theoretical predictions based on a magnetization-dependent Debye model. Also, a theoretical model based on the supertransferred process is presented which gives rise to a magnetization-dependent isomer shift, although the calculated effect is almost two orders of magnitude too small.

I. INTRODUCTION

THE shift of the center of a Mössbauer spectrum relative to the source has two components which arise in quite distinct ways. The isomer shift of the energy levels of the absorber with respect to the source is a result of the different electrostatic energies of these nuclei in the fields of the surrounding electrons. On the basis of a simple model, the isomer shift δ_i is given by[1]

$$\delta_i=\tfrac{2}{5}\pi Ze^2(R_e^2-R_g^2)[\psi_a^2(0)-\psi_e^2(0)],$$

where R_e and R_g are the nuclear radii of the excited and ground states and $\psi_a^2(0)$ and $\psi_e^2(0)$ are the *s*-electron densities at the absorbing and emitting nuclei. In Fe^{57}, $R_e<R_g$ so δ_i decreases with increasing *s*-electron density. The second-order Doppler shift may be regarded[2] as a consequence of the relativistic decrease in mass of the emitting nucleus. The emitted γ rays' energy is changed by δ_D, where in the Debye approximation

$$\delta_D=\frac{-9kTE}{4Mc^2}\left[\frac{1}{4}\frac{\Theta_D}{T}+2\left(\frac{T}{\Theta_D}\right)^3\int_0^{\Theta_D/T}\frac{x^3dx}{e^x-1}\right]. \qquad (1)$$

Here E is the energy of the γ ray, Θ_D is the Debye temperature, and in the case of a monoatomic lattice, M is the atomic weight. However, for a polyatomic lattice[3] in the low-temperature region, M is the average atomic weight of the atoms in the lattice $\bar{M}$, whereas in the high-temperature region M is the atomic weight of the Mössbauer atom M_a. These limits are approached when the phonon wavelengths are very much greater than, or very much less than, the lattice spacing. In any experiment the total Mössbauer spectrum shift δ_t which is actually measured is the sum of the isomer shift of the absorber relative to the source and the difference between the second-order Doppler shifts of the absorber and the source.

The *s*-electron density does not usually vary much with temperature so the temperature dependence of the total shift is generally assumed to be just the temperature dependence of δ_D. However, a careful investigation of the Mössbauer spectrum shift in iron[4] has revealed a discontinuity of 0.03 mm/sec in δ_t occurring in the region 0.3 degrees below the Curie point. Preston points out that his result might be at variance with the consensus that the magnetic transition in iron is higher than first order, and several other explanations have been proposed in terms of band theory.[5] It is therefore of interest to study and compare the behavior of the total shift in an insulator, particularly near the magnetic transition temperature.

An earlier investigation by Wertheim *et al.*[6] of FeF_3 showed the total shift to be continuous to within ±0.002 mm/sec. In this paper we report our measurements of δ_t in $HoFeO_3$ over a wide range of temperatures both above and below the Néel point T_N. Holmium orthoferrite has previously been studied by several authors[7,8] using the Mössbauer effect. Since $\bar{M}\simeq M_a$, the magnetization-dependent effects should not be obscured by the variation of M in Eq. (1).

II. EXPERIMENTAL PROCEDURE AND RESULTS

The $HoFeO_3$ absorber was prepared from 99.9% pure Ho_2O_3 and Fe_2O_3 and it was enriched with $Fe^{57}{}_2O_3$, so that 27% of the iron was the Mössbauer isotope. An x-ray photograph agreed with the published powder pattern.[9]

More than 100 spectra were taken in the range 99–875°K using two "Elron" spectrometers, one operated at constant velocity and the other at constant acceleration in conjunction with a multichannel

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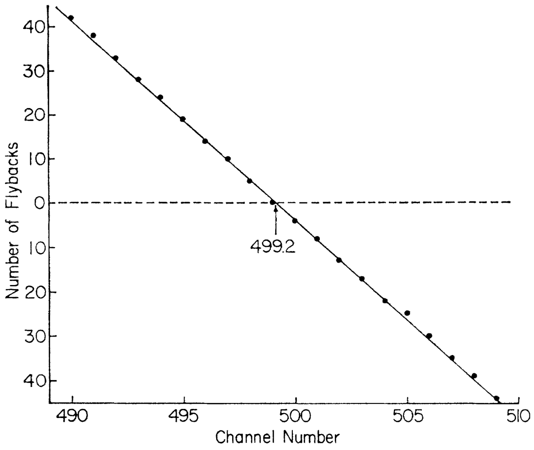

FIG. 1. Plot of the number of flybacks in the channels close to the zero in the constant velocity mode to find the exact zero position.

analyzer. Any error in the measured total spectrum shift due to nonlinearity of the systems was found to be less than 0.002 mm/sec from calibration spectra with an iron foil. In order to measure the total Mössbauer spectrum shift accurately, it is necessary to keep track of the zero drift, and to collect the spectra in a time in which the zero moves by no more than 0.002 mm/sec when operating at constant velocity. Two methods of determining the zero were used in this experiment. While operating at constant velocity, the number of flybacks in each of the 20 channels around the zero was counted electronically and the exact position of the zero was found to within a tenth of a channel (±0.001 mm/sec) by interpolation. A typical result is shown in Fig. 1. The alternative, and somewhat less accurate method, was to use a sodium-ferrocyanide marker at room temperature placed between the cryostat or furnace and the counter. The quadrupole splitting in this material is so small that its spectrum is essentially a single peak relative to which the center of the $HoFeO_3$ spectrum is measured. This method is most useful well below T_N, where it barely overlaps the center lines of the orthoferrite spectrum and the peak position could be determined to within 0.003 mm/sec. Temperature stability was typically ±1°K below room temperature and ±0.5°K above. An upper limit for temperature inhomogeneity was deduced from measurements of the line broadening just below T_N. Because

$$\frac{dx}{dT}=\frac{dx}{dH}\frac{dH}{dT},$$

where x is the peak position and H is the hyperfine field, we can write

$$\Delta\Gamma\simeq\Delta T\frac{dx}{dH}\frac{dH}{dT}.$$

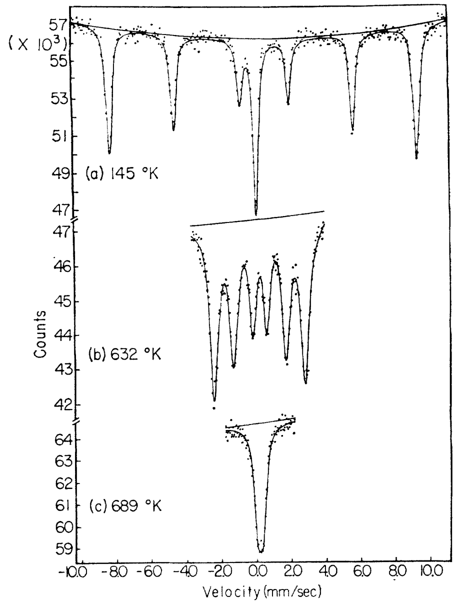

FIG. 2. Typical Mössbauer spectra of $HoFeO_3$ (a) at constant acceleration and (b) and (c) at constant velocity.

A plot of the line broadening $\Delta\Gamma$ as a function of dH/dT has slope $\Delta T(dx/dH)$, where ΔT is the temperature inhomogeneity. This procedure gave an upper limit of 2°K for the temperature inhomogeneity, but the true value may be smaller as there can be a temperature-dependent broadening due to impurities and relaxation effects[10] in this region.

Some typical spectra are shown in Fig. 2; (a) is a spectrum taken at constant acceleration with the sodium-ferrocyanide marker, whereas (b) and (c) were taken at constant velocity and the zero was measured by counting flybacks. The velocity scale is relative to the source, 10 mCi of Co^{57} in a chromium matrix, and its temperature was constant to ±2°K. The data were analyzed in the usual way by fitting Lorentzians to the peaks by the method of least squares. Above T_N the spectrum is a close doublet due to the quadrupole interaction which gives a splitting of 0.309±0.005 mm/sec. When fitting these doublets, the two peaks were constrained to have the same intensities and full widths at half-maximum. Otherwise no constraints were used except in the case of the two center lines of the spectra taken below T_N with the sodium-ferrocyanide marker which were similarly constrained.

The total shift is plotted against temperature in Fig. 3. Many of the points shown are averages from two spectra taken at the same temperature. Some typical errors are indicated; thay are obtained from the error in the least-squares fit to the peak positions and the error in the position of the zero.

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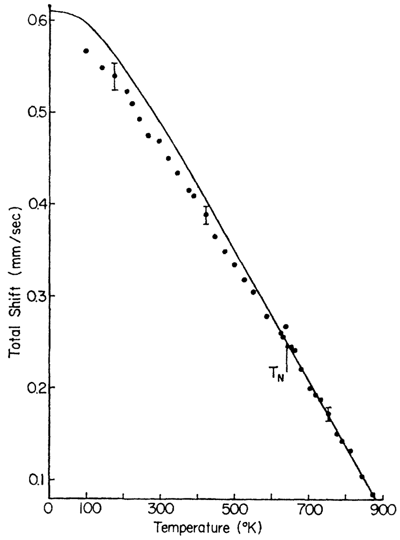

FIG. 3. Temperature variation of the total Mössbauer spectrum shift. The theoretical curve for a Debye temperature of 457°K is drawn to fit the data in the paramagnetic region.

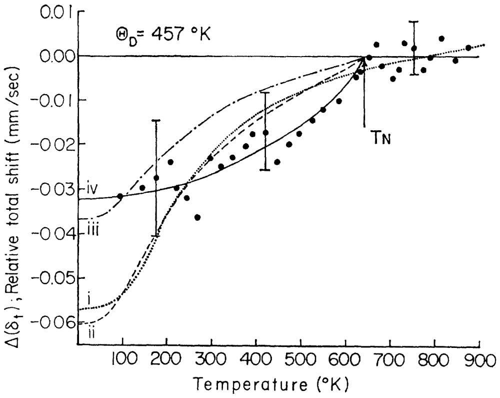

FIG. 4. Total shift data relative to the $\Theta_D=457$°K curve. Theoretical curves are drawn (i) for $\Theta_D=720$°K, (ii) for $\Theta_D'(0)=676$°K, (iii) for $\Theta_D'(0)=591$°K, and (iv) showing a variation proportional to μ^2.

The Néel temperature T_N was found to be 642.7°K from an H^3 versus T plot for $T/T_N>0.995$. This agrees well with 642.5°K, the value obtained by thermal scanning, and is fairly close to the result (639°K) found by Eibschutz *et al.*[8] However, we were able to fit our spectra with broadened outside lines, but without paramagnetic peaks, right up to 640.0°K.

The Debye temperature Θ_D was deduced from the variation of the total absorption as a function of temperature[11] in two different ranges. Above T_N, in the range 647–875°K, we found $\Theta_D=457\pm30$°K while below T_N in the range 320–550°K, we obtained $\Theta_D=540\pm30$°K. These errors are two standard deviations from a least-squares fit to a straight line of a ln (absorption area) versus T plot, and do not take into account any possible systematic error, or inadequacy of the Debye model.

The slope of the δ_t versus T plot for $T>T_N$ was found to be $(-7.09\pm0.09)\times10^{-4}$ mm/sec deg. The slope predicted by Eq. (1) in the same range, taking $\Theta_D=457$°K and $M=M_a$, is -7.17×10^{-4} mm/sec deg. Equation (3) then fits the data in the paramagnetic region, and the curve for $\Theta_D=457$°K is drawn in Fig. 3.

III. DISCUSSION

It can be seen from Fig. 3 that every point but one in the antiferromagnetic region lies below the curve for $\Theta_D=457$°K. They are shown on an expanded scale in Fig. 4, where the departure from the Debye theory for $\Theta_D=457$°K is plotted. We attempted to fit all the data to a single Debye temperature, and curve (i) in Fig. 4 is the best fit. Although it is within the experimental error of much of the data, curve (i) appears to have the wrong shape, and corresponds to a Debye temperature of 720°K, which is entirely different to either of the measured values. The important feature of the plot in Fig. 4 is that the departure from the Debye theory starts at the magnetic transition temperature. This suggests that the observed effect is associated with the degree of magnetic order in the system and not simply the inadequacy of the Debye theory in describing the phonon spectrum. It can also be seen, by extrapolating the data in the regions above and below T_N, that any discontinuity in δ_t is less than 0.003 mm/sec.

The observed effect could have two possible causes: (1) A dependence of the second-order Doppler shift on the degree of magnetic order in the system or (2) a dependence of the isomer shift (s-electron density) on the degree of magnetic order.

Bashkirov and Selyutin[12] have calculated the temperature dependence of the second-order Doppler shift in crystals containing exchange-coupled magnetic ions. On the basis of the Debye model they deduce an expression for δ_D as a function of temperature and spin order which may be written

$$\delta_D(T,\Theta_D')=\frac{-9kTE}{4Mc^2}\times\left[\frac{1}{4}\frac{\Theta_D'}{T}+2\left(\frac{T}{\Theta_D'}\right)^3\int_0^{\Theta_D'/T}\frac{x^3dx}{e^x-1}\right], \qquad (2)$$

where

$$\Theta_D'=\Theta_D(1+B)^{1/2}. \qquad (3)$$

The change in Θ_D' due to magnetic order is given by the parameter B, where

$$B=-(8\pi^2\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle a^2/v^2M)J_e''(a).$$

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By assuming a molecular-field model, this can be written

$$B = B_0\mu^2, \tag{4}$$

where a is the distance between neighboring magnetic ions, v is the velocity of sound in the lattice, $J_e''(a)$ is the second derivative of the exchange integral, and μ is the reduced sublattice magnetization.

Equation (2) is similar to (1) except that the spin ordering is allowed for by an effective Debye temperature Θ_D', which appears instead of Θ_D for the Mössbauer ions in the ferromagnetic state.

These authors suggest that $B > 0$ both in ferromagnets and antiferromagnets and that $B_0 \simeq 1$, i.e., they expect that Θ_D' will be considerably greater than Θ_D in the low-temperature region where $\mu^2 \simeq 1$ and that δ_D will be 0.01 to 0.1 mm/sec less than it would be if the behavior above the magnetic transition temperature could be extrapolated to $T = 0$. It is worth noticing that unless the lattice parameter changes abruptly at T_N, no discontinuity in the second-order Doppler shift is predicted by their theory because there is no discontinuity in $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$.

Curves (ii) and (iii) in Fig. 4 represent attempts to fit the data, assuming that the only magnetization-dependent effect is the second-order Doppler shift. Curve (ii) is the best fit obtainable by adjusting B_0 in Eq. (4) and taking $\Theta_D = 457°\text{K}$; $B_0 = 1.2$ and $\Theta_D'(0) = 676°\text{K}$. This is much higher than the Debye temperature (390°K) deduced from low-temperature specific-heat measurements in another orthoferrite.[13] As the corresponding average value of Θ_D' in the range 320–550°K is 597°K, and is not consistent with the measured value of Θ_D' ($540 \pm 30°\text{K}$) in this range, we have also shown curve (iii) for $B_0 = 0.67$, which corresponds to the Θ_D' actually measured. However, this curve lies just outside the experimental error of most of the points and does not seem to have the observed shape. We deduce that the data cannot be quite satisfactorily explained solely in terms of a magnetization-dependent second-order Doppler shift.

Curve (iv) is an attempt to fit the data completely with a term proportional to μ^2. This fits the data well over the whole range with $\Delta(\delta_i) = -0.035\mu^2$. A dependence proportional to the magnetization works equally well. By using the isomer-shift calibration of Walker *et al.*,[4] this would mean a change in the s-electron density of $0.069 a_0^{-3}$.

The dependence of the s-electron density on the degree of magnetic order could arise from a change in the covalency and overlap effects in going from the paramagnetic to the magnetically ordered state. It has been shown[14,15] that covalency and overlap effects can give rise to a transfer of spin from a metal ion ($M1$) via the ligand to another metal ion ($M2$). The change in the spin or charge density due to this effect is proportional to

$$A_\sigma^2 \Big[\sum_{n=1}^{3} S_{p,ns}\phi_{ns}(0)\Big]^2 \tag{5}$$

using the notation and approximations made by Šimánek *et al.*[16] Here $S_{p,ns} = \langle p | \phi_{ns} \rangle$, and ϕ_{ns} refers to the core s orbitals associated with $M1$. In the magnetically ordered state at 0°K, the spin associated with the orbitals in Eq. (5) is that of $M2$, i.e., antiparallel to the spin of $M1$, whereas in the paramagnetic state these orbitals have no net spin dependence. Because $\phi_{ns}^{\uparrow}(0) \neq \phi_{ns}^{\downarrow}(0)$ and also $\langle p | \phi_{ns}^{\uparrow} \rangle \neq \langle p | \phi_{ns}^{\downarrow} \rangle$, it is easy to see that the charge transferred in the magnetically ordered state can be different from that in the paramagnetic state. A calculation of this effect, however, yielded a value two orders of magnitude smaller than the observed value and of the opposite sign. The calculation is, however, very sensitive to the tail region of the core s orbitals which could in these materials be considerably different from the free-ion wave functions used.

Effects arising from the 6% difference between $\bar{M}$ and M_a have been neglected throughout. We would expect that at 0°K there would be a contribution to $\Delta(\delta_i)$ of at most -0.007 mm/sec.

We conclude that there are measurable magnetic effects on the total Mössbauer spectrum shift in an insulator and we have shown that a contribution to the isomer shift proportional to μ^2 fits the data satisfactorily although a magnetization-dependent second-order Doppler shift cannot be excluded. It would be of interest to repeat these studies on other magnetically ordered insulators to see if the effect is general.

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