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Thermal Shift of a Mössbauer Gamma Ray at a Magnetic Phase Transition

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The thermal shift of the ^{57}Fe Mössbauer γ ray in rhombohedral FeF$_3$ gives a weak indication of a magnetization-dependent Debye temperature. A small isomer-shift discontinuity exists at the transition to cubic structure at high temperature.

Effects of magnetic phase transitions on the Mössbauer effect thermal shift in insulators have recently received both theoretical[1] and experimental attention.[2] We have examined this effect in the compound FeF$_3$ and find a small magnetization-dependent change in the Debye temperature below the Curie point. This result is in accord with theoretical estimates[1] but differs from experimental results in another similar system.[2]

The thermal shift δE_T arises through the second-order relativistic Doppler effect from the thermal motion of atoms in a solid. It is related to the kinetic energy of atoms, and therefore to the lattice heat capacity[3] and internal energy per atom, U, by the equation

$$\delta E_T/E = -U/2Mc^2, \tag{1}$$

where E is the energy of the γ ray and c the velocity of light. The internal energy should include the zero-point energy U_0 in addition to the usual expression. In the Debye approximation, the zero-point energy is

$$U_0 = \tfrac{9}{8} k\Theta, \tag{2}$$

where Θ is the Debye temperature. The temperature-dependent term is

$$U = 9kT(T/\Theta)^3 \int_0^{\Theta/T} x^3(e^x - 1)^{-1} dx . \qquad (3)$$

Inserting into Eq. (1) yields

$$\frac{\delta E_T}{E} = -\frac{3kT}{2Mc^2}\left[\frac{3}{8}\frac{\Theta}{T} + 3\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} x^3(e^x - 1)^{-1} dx\right], \qquad (4)$$

which is readily evaluated using a tabulation of the integral.[4] In the region where $T > \frac{1}{3}\Theta$ the expression[5]

$$\delta E_T/E \approx -(3kT/2Mc^2)(1 + \Theta^2/20T^2) \qquad (5)$$

provides a useful approximation to Eq. (4).

It should be noted, however, that the corresponding expression evaluated in the Einstein model differs only in a numerical factor

$$\delta E_T/E \approx -(3kT/2Mc^2)(1 + \Theta_E^2/12T^2). \qquad (6)$$

It is therefore immediately apparent that the thermal shift is not sensitive to the details of the vibrational spectrum in the region where $T > \frac{1}{3}\Theta$.

A measured shift δE is expressed relative to a reference substance and therefore contains a contribution from the isomer shift δE_I:

$$\delta E = \delta E_I + \delta E_T . \qquad (7)$$

The isomer shift will, in general, also have an explicit temperature dependence traceable to the effect of thermal expansion on the electronic charge density at the nucleus. In the high-temperature region we approximate this by the linear behavior

$$\delta E_I = \delta E_I^0 + aT . \qquad (8)$$

The coefficient a can be estimated from the pressure dependence of the isomer shift, the coefficient of thermal expansion, and the bulk modulus.[5] (It is generally assumed that the shift with pressure is due to changes in the electronic wave functions rather than to changes in the Debye temperature, because the latter can account for only a small part of the measured effect.)

Combining Eqs. (5), (7), and (8) we obtain

$$\frac{\delta E}{E} + \left(\frac{3k}{2Mc^2} - \frac{a}{E}\right)T = \frac{\delta E_I^0}{E} - \frac{3k\Theta^2}{40Mc^2T} , \qquad (9)$$

which shows that a plot of the left-hand side of the equation against T^{-1} will be a straight line provided the Debye temperature is independent of temperature and provided the above approximations are valid. The intercept of this plot gives the isomer shift in the *absence of all atomic motion*. The square root of the slope gives the Debye temperature. Sudden changes in isomer shift or Debye temperature should be immediately apparent in such a plot, but they are expected only at first-order phase transitions.

At a magnetic second-order transition, theory[1] indicates that the Debye temperature will vary as

$$\Theta' = \Theta(1 + B_0\mu^2)^{1/2} , \qquad (10)$$

where B_0 is generally positive and μ is the reduced sublattice magnetization. The isomer shift should therefore be continuous at the Curie point. The slope of the plot is proportional to $1 + B_0$ at low temperature where the magnetization is saturated, and should show a transitional region near the Curie point.

The compound FeF_3 has been the subject of a number of Mössbauer studies concerned with the critical point magnetization.[6–9] The isomer shift has also been shown to be continuous at the Curie point[7] but the possibility of a change in its Debye temperature has not been previously examined. The compound has a rhombohedral structure at room temperature[10] and a crystallographic phase transition to a cubic structure at 410 °C.[11] The material used in this study was similar to that used in our previous investigation.[7]

Data were taken with conventional constant-acceleration spectrometer using a ^{57}Co in palladium source. All shifts are expressed relative to the midpoint of the absorption spectrum of metallic iron at 298 °K. The absorbers were polycrystalline powders. Two separate systems were used for temperature control. The low-temperature data were taken in a vacuum Dewar using an adjustable heat leak and a resistive heater controlled by a feedback system.[12] Temperatures were measured with copper-constantan thermocouples. Data above room temperature were taken in a vacuum furnace insulated with multiple concentric radiation shields provided with beryllium windows. Temperature was controlled with a platinum-platinum 10% rhodium thermocouple and sample temperature measured with a chromel-alumel couple. The temperature stability was better than ±0.1 °K, but absolute sample temperature is not known to better than ±0.5 °K.

A major concern in these experiments arises from the fact that the shifts at low temperature must be determined from spectra with large magnetic hfs splitting. This puts severe requirements on the linearity and zero-point stability of the Doppler spectrometer. These were checked with absorption spectra of metallic iron.

The results of our measurements are shown in Fig. 1. The curve through the points was constructed using the Debye expression for the thermal shift and the parameters obtained from the analysis in Fig. 2. The data are the result of a series of interleaved runs, usually taken with increasing temperature. After the highest-temperature data were taken the sample showed evidence of a small amount of decomposition, but the properties of the undecomposed material were un-

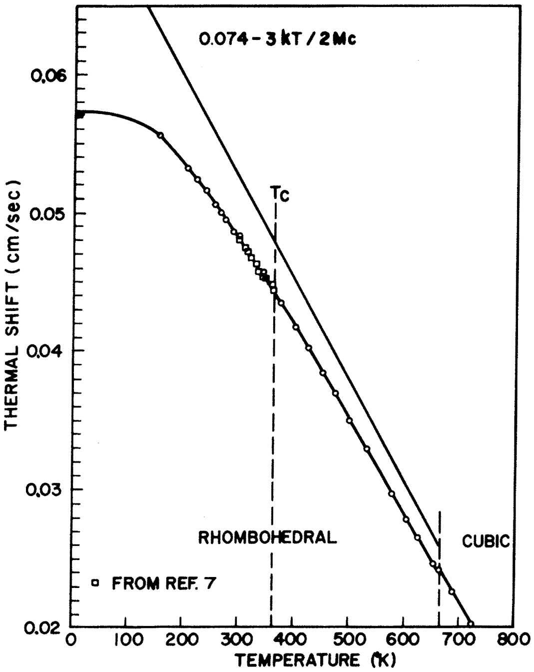

FIG. 1. Thermal shift of the Mössbauer γ ray of ^{57}Fe in FeF_3 relative to metallic iron at 298 °K.

changed. Data from Ref. 7, recalculated with respect to the iron reference, are also included. The small discontinuity at 670 °K is due to the crystallographic phase transition.[11] It has not been determined whether the origin of the discontinuity lies in the thermal or isomer shift.

In Fig. 2, the same data have been plotted according to Eq. (9) with $a = 0$. The scale of the ordinate has been greatly expanded because this plot shows *only the deviation* of the data *from the classical shift* of $3kT/2Mc$, which contains the information on the Debye temperature. The curve through the points is the result of evaluating Eq. (4) for $\Theta = 615$ °K. The fit is adequate and gives no indication of a break at the Curie point. The dashed line is obtained for the same parameters from Eq. (5). (A straight line of somewhat smaller slope and intercept fits the data within the experimental uncertainty.)

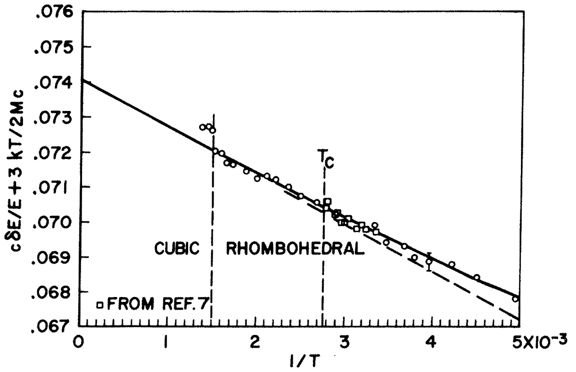

FIG. 2. Plot of data according to Eq. (9) with $a = 0$(1/T in °K^{-1}). The curve through the data was computed using the exact expression with $\Theta = 615$ °K and $c\delta E_I/E = 0.074\,06$ cm/sec. The probable errors indicated arise largely from temperature uncertainty above T_c and from line position uncertainty below T_c.

Up to this point the temperature coefficient of the isomer shift has been neglected. We have estimated its magnitude using the pressure coefficient of the shifts of K_3FeF_6 and $FeF_3 \cdot 3H_2O$, which are $\sim 8 \times 10^{-5}$ cm/sec kbar,[13] since direct measurements on FeF_3 are not available. The bulk modulus was estimated to be 600 kbar and linear thermal expansion coefficient was taken to be $10^{-5}\,(°\mathrm{K})^{-1}$. The resulting temperature coefficient for the isomer shift is 0.15×10^{-5} cm/sec °K, which is much smaller than the second-order Doppler shift of 7.25×10^{-5} cm/sec °K. The uncertainty in the isomer-shift coefficient is, however, at least a factor of 2.

The data are replotted in Fig. 3 with this correction included. They are now better fitted by expression 3.16 of Ref. 1, using the known temperature dependence of the sublattice magnetization.[7,9] This fit yields a Debye temperature in the paramagnetic phase of 506 °K and a coefficient B_0 of 0.25 ± 0.15. The magnitude of B_0 is of the order expected according to Ref. 1. It should be noted, however, that the detectability of the effect depends largely on the highly uncertain isomer-shift correction. We therefore assign a value of (506 ± 80) °K to the effective Debye temperature of the iron atoms. The relation of such a Debye temperature to that of the crystal as a whole has been discussed by Iosilevskii[14] and will not be consid-

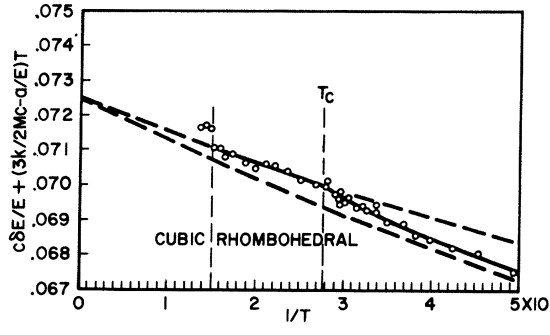

FIG. 3. Plot of the data with estimated isomer-shift temperature coefficient included (1/T in °K^{-1}). The solid curve is based on the theory of Ref. 1.

ered here. The Debye temperatures of CaF_2 (474 °K) and FeS_2 (630 °K) indicate that the present value is not unreasonable.

Present results are in accord with the change in the Debye temperature due to magnetic ordering calculated in Ref. 1. They are sufficiently uncertain, however, so that independent measurements of the Debye temperature of FeF_3 by x-ray scattering would be desirable. FeF_3 does not have the anomalous behavior found in $HoFeO_3$. Experiments on other systems, especially those in which the temperature coefficient of the isomer shift can be more accurately obtained, are needed to confirm these results.

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