Mössbauer Effect Study of FeSb₂

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An analysis of the Mössbauer effect spectrum of a well-characterized sample of the marcasite-type compound FeSb₂ shows that the unusual temperature dependence of the quadrupole splitting is a result of the promotion of electrons across an energy gap. The fitting of the data (taken over a temperature range of 6.4–560°K) to a derived function gives a value of 0.033(1) eV for this energy separation, in good agreement with the value derived from electrical conductivity measurements (4). An analysis of the isomer shift data in terms of the Debye approximation yields a value of 380°K for the Debye temperature.

Introduction

Temperley and Lefevre (*1*) have reported a significant change in the Mössbauer effect quadrupole splitting with temperature for FeSb₂ which is not observed for similar compounds with the marcasite structure type: FeS₂, FeSe₂ and FeTe₂ (*1*) and FeAs₂ (*2*). A tentative explanation of this anomaly has been offered by Holseth and Kjekshus (*3*), who, in a single-crystal X-ray diffraction analysis, determined that FeSb₂ lacks the mirror plane of the previously assumed marcasite structure-type (*Pnnm*) and crystallizes in the space group *Pnn2*. The destruction of this mirror plane results in the shifting of the iron atoms from the center of the coordinating Sb₆ polyhedra, which could give rise to the observed temperature variation of the quadrupole splitting with changes in the structural parameters.

In conjunction with an experimental (*4*) and theoretical (*5*) investigation of the magnetic and electrical properties of well-characterized single crystals of FeAs₂ and FeSb₂, we have performed a detailed Mössbauer effect investigation of FeSb₂ over the temperature range 6.4–560°K and are able to show that the temperature dependence of the quadrupole splitting is a result of an electronic process involving the thermal population of an empty conduction band. An analogous temperature dependence of the quadrupole splitting is well known for Fe²⁺ ions (*6*) and has been observed in the intermetallic compound FeSi (*7*). A detailed analysis of the isomer shift is made within the Debye approximation.

Experimental

Single crystals of FeSb₂ (generously supplied by Professor A. Wold (*4*)) were carefully ground under a dry nitrogen atmosphere. The samples used for Mössbauer effect measurements contained 55 mg/cm² FeSb₂ (corresponding to 10 mg/cm² of iron).

The ⁵⁷Fe Mössbauer effect was measured with a commercial spectrometer (Model NS-1, Nuclear Science and Engineering Corporation) operating in the constant acceleration mode. Data were collected with a 400-channel analyser operating in time-sequence scaling mode. The source (15 mCi of ⁵⁷Co diffused into palladium metal) and drive were calibrated against a single crystal of sodium nitroprusside (National Bureau of Standards, Standard Reference Material No. 725). The quadrupole splitting for sodium nitroprusside was taken as 1.7048 ± 0.0025 mm/sec (*8*); isomer shifts are reported with respect to the zero position of this standard. The data were reduced by a nonlinear least-squares fit to the product of a series of absorption peaks having Lorentzian shapes superposed on a parabolic base line (a result of our particular drive geometry). All variables (peak position, height, and half-width) were allowed to vary independently.

Cryogenic measurements were made in a variable-temperature Dewar with the source at room temperature; temperature control was within $\pm 0.5°K$ for temperatures above and $\pm 0.01°K$ below liquid nitrogen temperatures. Measurements above room temperature were made with the sample mounted in a small Kanthal-wound furnace with temperature control within $\pm 1.0°K$. The powdered sample was mounted between two beryllium discs (0.010 mil thick) to effect good thermal equilibrium.

Results and Discussion

Our data for $FeSb_2$ over the temperature range 6.4–560°K are presented in the table and plotted in the figure. These data are in good agreement with the previously reported data (1) for room temperature and liquid nitrogen temperature and are characteristic of covalently-bonded

TABLE I

$FeSb_2$ Mössbauer Effect Parameters[a]

T, °K	Isomer Shift[b]	Quadrupole Splitting
6.4	0.832	1.575
20	0.833	1.576
40	0.834	1.578
60	0.837	1.571
77	0.826	1.557
97	0.821	1.560
113	0.804	1.551
137	0.799	1.514
159	0.788	1.437
195	0.767	1.394
210	0.755	1.370
229	0.756	1.339
250	0.736	1.308
273	0.729	1.283
296	0.710	1.268
340	0.670	1.230
400	0.635	1.172
454	0.598	1.135
500	0.558	1.102
527	0.544	1.089
560	0.521	1.065

[a] All values in mm/sec with an estimated error of 0.006 mm/sec.
[b] Relative to sodium nitroprusside.

iron in an asymmetric environment. Peak half-widths (FWHM) are on the order of 0.28 mm/sec.

The solid curves represent least-squares fits to the functions derived below and the open circles are the experimental points. No evidence for magnetic ordering was found, in agreement with the most recent magnetic susceptibility measurements (4) and neutron diffraction studies (9).

A. Isomer Shift. Within the Debye approximation the isomer shift is given as (10–12)

$$\delta E(T) = \delta E_C - (3kET/2MC^2)[(3/8)\alpha + f_D(\alpha)], \tag{1}$$

where $\alpha = \theta_D/T$, the reduced Debye temperature, and E_C is the isomer shift at 0°K neglecting the zero point Doppler shift contribution $(-3kET/2MC^2)[(3/8)\alpha]$.

The Debye integral $f_D(\alpha)$ is given as

$$\frac{3}{\alpha^3} \int_0^\alpha x^3 (e^x - 1)^{-1} dx$$

and can be evaluated as follows:

$$\int_0^\alpha x^3 (e^x - 1)^{-1} dx$$

$$= \int_0^\infty x^3 (e^x - 1)^{-1} dx - \int_\alpha^\infty x^3 (e^x - 1)^{-1} dx.$$

Contour integration of the first integral gives

$$\int_0^\infty x^3 (e^x - 1)^{-1} dx = \frac{\pi^4}{15}.$$

Integration of the second integral by parts yields

$$\int_\alpha^\infty x^3 (e^x - 1)^{-1} dx$$

$$= -\alpha^3 \ln(1 - e^{-\alpha}) - 3 \int_\alpha^\infty x^2 \ln(1 - e^{-x}) dx.$$

The resulting integral is evaluated by expanding the natural logarithm and integrating the terms of the series as follows:

$$\int_\alpha^\infty x^2 \ln(1 - e^{-x}) dx = \int_\alpha^\infty \sum_{n=1}^\infty -\frac{1}{n} x^2 e^{-nx} dx$$

$$= -\sum_{n=1}^\infty \left[\frac{\alpha^2}{n^2} + \frac{2\alpha}{n^3} + \frac{2}{n^4} \right] e^{-n\alpha}.$$
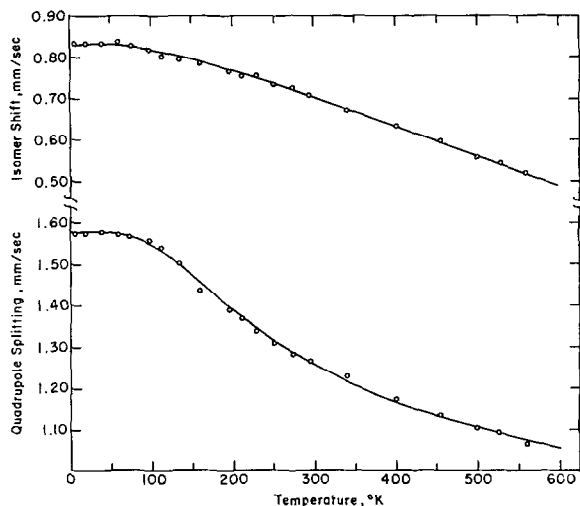
FIG. 1. Top: Isomer shift *vs.* temperature. The open circles are the experimental points; the solid line is a least-squares fit to Eq. (2) (see text).

Bottom: Quadrupole splitting *vs.* temperature. The open circles are the experimental points; the curve is a least-squares fit to Eq. (5) (see text).

Combining the above equations into Eq. (1) gives the following expression for the temperature dependence of the isomer shift:

$$\delta E(T)$$
$$= \delta E_C - \frac{3kET}{2MC^2}\left\{\frac{3}{8}\alpha + \frac{3}{\alpha^3}\left[\frac{\pi^4}{15} + \alpha^3 \ \ln(1 - e^{-\alpha})\right.\right.$$
$$\left.\left. - 3\sum_{n=1}^{\infty}\left(\frac{\alpha^2}{n^2} + \frac{2\alpha}{n^3} + \frac{2}{n^4}\right)e^{-n\alpha}\right]\right\} \qquad (2)$$

The high temperature isomer shift data for FeSb$_2$ ($T > 270°$K) was fit to a linear function, the intercept (0.921 mm/sec) taken as an estimate for δE_C. The slope of the high temperature linear fit [-7.18×10^{-4} (mm/sec/deg)] should be compared with the classical value for 14.4 keV ^{57}Fe γ-rays [-7.25×10^{-4} (mm/sec/deg)]. An estimate for θ_D is obtained at 0°K from Eq. (2) as

$$\theta_D = \frac{\delta E_{(o)} - \delta E_C}{-(9/16)\,(kE/MC^2)} = 327°K.$$

The entire set of isomer shift data was then fit to Eq. (2) using the estimates for δE_C and θ_D as starting points. The resulting parameters are: $\theta_D = 380(5)°$K and $\delta E_C = 0.937(4)$ mm/sec.

The fact that the slope in the high temperature region is not equal to the classical limit could result from either a temperature-dependent Debye temperature or an additional functional dependence of the isomer shift with temperature due to a lattice contraction. An attempt to fit the data to a function which included terms of this type gave essentially identical values for θ_D and δE_C.

B. Quadrupole Splitting. In general, the quadrupole splitting as a function of temperature, $\Delta E(T)$, can be expressed as the sum of the contribution of the valence electrons, ΔE_{val} (T), and the lattice contribution, ΔE_{lat} (T)

$$\Delta E(T) = \Delta E_{val}(T) + \Delta E_{lat}(T) \qquad (3)$$

In the molecular orbital model for marcasite-type compounds proposed by Goodenough (5) the relevant energy levels consist of a filled b-band separated from a higher energy (empty) $a_{\parallel}$-band by an energy gap. This scheme is similar to that proposed by Brostigen and Kjekshus (*13*) and allows a thermal population of the higher energy level. The four valence electrons assigned to the iron atom occupy the lower level at 0°K (*4*). If the energy between these two levels (ϵ) is large relative to the spin-orbit coupling then the valence electron contribution to the quadrupole splitting at a temperature T can be approximated (*14*) by

$$\Delta E_{val}(T) = \Delta E_{val}(O)\tanh\left[\frac{\epsilon}{2kT}\right] \qquad (4)$$

where $\Delta E_{val}(O)$ is the valence electron contribution to the quadrupole splitting at $0°K$.

For many compounds the lattice contribution to the total quadrupole splitting is assumed to be constant with temperature provided that the lattice changes isotropically with temperature. However, if there is an anisotropic lattice expansion or contraction, a temperature-dependent lattice contribution must be included in Eq. (3). Since we are able to fit our data to a function which contains a linear temperature-dependent term (vide infra), by introducing this term and substituting Eq. (4) into Eq. (3), the total quadrupole splitting is given by

$$\Delta E(T) = \Delta E_{val}(O)\tanh\left[\frac{\epsilon}{2kT}\right]$$
$$+ \Delta E_{lat}(O) + \frac{d[\Delta E_{lat}(T)]}{dT} \cdot T. \quad (5)$$

Furthermore, if there is no temperature-dependent contribution to ΔE_{val}, which would be the case if ϵ is large relative to kT, Eq. (5) reduces to

$$\Delta E(T) = \Delta E_{val}(O) + \Delta E_{lat}(O) + \frac{d[\Delta E_{lat}(T)]}{dT} \cdot T,$$

assuming that there still exists a linear temperature-dependent contribution to ΔE_{lat}.

The quadrupole splitting vs. temperature data (cf. Figure) has been fit to Eq. (5). The resultant parameters are:

$$\Delta E_{val}(O) = 0.716(4)\,\text{mm/sec}$$

$$\Delta E_{lat}(O) = 0.864(4)\,\text{mm/sec}$$

$$\frac{d[\Delta E_{lat}(T)]}{dT} = -0.472(4) \times 10^{-4}\,\text{mm/sec/deg}$$

$$\epsilon = 0.033(1)\,\text{eV}$$

The activation energy determined from the Mössbauer effect measurements on a polycrystalline sample will be a function of the activation energies along the different crystallographic axes for an anisotropic sample. This functional activation energy is calculated by integrating the product of the activation energy for a particular direction and the relative orientation distribution function over all possible angles. For the case of axial symmetry, the average activation energy ($\bar{\epsilon}$) is given as a function of the parallel and perpendicular components, $\bar{\epsilon} = (1/3)\epsilon_{\parallel} + (2/3)\epsilon_{\perp}$. Our value of $0.033(1)$ eV for the electronic energy gap is in good agree-

ment with the value of ~ 0.026 eV derived from conductivity measurements.

Our rationale for including a linearly temperature-dependent lattice contribution to the total quadrupole splitting is as follows. Both in $FeSb_2$ and the isostructural $FeAs_2$ the c/a and c/b axial ratios increase with temperature (15). Our preliminary Mössbauer effect data for $FeAs_2$ indicate a slight linear decrease in the quadrupole splitting over the temperature range 77–298°K which, since $FeAs_2$ has a significantly higher band gap energy (0.22 eV) (4), should be due solely to a lattice contribution to the quadrupole splitting. In other words, the valence electron contribution to the observed quadrupole splitting is essentially constant over this temperature range. It is instructive to note that the slope of $d[\Delta E_{lat}(T)]/dT$ for $FeSb_2$ is negative; the lattice contribution to the quadrupole splitting is decreasing with increasing temperature which parallels an increase in the c/a and c/b axial ratios with increasing temperature, an effect which reduces the distortion of the ligand field. The slope (-0.472×10^{-4} mm/sec/deg) is of comparable magnitude to that in $FeAs_2$ (-1.1×10^{-4} mm/sec/deg). An attempt to fit the data to a function lacking the linear temperature-dependent term gave poor results.

We feel that the tentative structural explanation proposed by Holseth and Kjekshus (3) can be discounted as a contributing factor to the observed temperature-dependence of the quadrupole splitting. In a further paper (16), FeS_2-m was also shown to crystallize in the space group $Pnn2$; that is, it also lacks the mirror plane of the assumed $Pnnm$ space group of the marcastie structure-type. However, Mössbauer effect measurements (1) on FeS_2-m indicate a normal temperature dependence of the quadrupole splitting. It is, therefore, unreasonable to assume an "off-centeredness" contribution to the quadrupole splitting in $FeSb_2$ and not in other compounds of this structure type. Although a complete single crystal X-ray diffraction analysis has not been reported for $FeAs_2$, it is not unreasonable to assume that it also adopts the space group $Pnn2$.

Acknowledgment

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