JOURNAL OF SOLID STATE CHEMISTRY 5, 136-143 (1972)

Preparation and Properties of $FeAs_2$ and $FeSb_2$*

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Received November 5, 1971

Single crystals of $FeAs_2$ and $FeSb_2$ were prepared by chemical vapor transport using chlorine as the transporting agent. Electrical and magnetic measurements have been made on well-characterized samples. $FeAs_2$ was found to be a diamagnetic semiconductor with a band gap of 0.22 eV. $FeSb_2$ has an extremely narrow band gap and shows unusual electrical and magnetic properties. Aproposed band model is used to explain the experimental results.

Introduction

There have been several recent studies (*1–3*) concerning the preparation and properties of several transition metal compounds crystallizing with the pyrite structure. A similar group of compounds, with the marcasite structure, has also received considerable attention (*4–10*). Recently, several theoretical models have been proposed (*11–13*) in order to explain the experimental data obtained for both groups of compounds. However, the properties of $FeAs_2$ and $FeSb_2$, crystallizing with the marcasite structure, are inconsistent with these models. Previous measurements have been made on either polycrystalline materials or natural minerals and the difficulty may be related to the purity of the products.

Holseth and Kjekshus (*14*, *15*) have reported the space group of $FeAs_2$ to be P_{nnm} $FeSb_2$ space group $P_{nn}2$, is similar in structure to $FeAs_2$ but lacks the mirror plane perpendicular to the *c*-axis. Hulliger (*4*) has reported that both $FeAs_2$ and $FeSb_2$ are semiconductors with band gaps of 0.2 and 0.05 eV, respectively. However, Dudkin and Vaidanich (*5*) reported a band gap of 0.34 eV for $FeSb_2$; their results have not been substantiated. In a later study, Johnston et al. (*6*) reported on the electrical properties of a natural mineral specimen of $FeAs_2$ and a synthetic sample of $FeSb_2$. Unfortunately their measurements were made on impure samples and, therefore, may be unreliable.

Hulliger (*12*), and Brostigen and Kjekshus (*13*) have proposed a band scheme from which they predict that marcasites having the d^4 configuration should be diamagnetic. However, $FeAs_2$ has been reported (*7*, *8*) to show weakly temperature dependent paramagnetism. This behavior was attributed by Wintenberger(*7*) to be caused by the presence of impurities. $FeSb_2$ was reported by both Rosenqvist (*9*) and Holseth and Kjekshus (*8*) to be antiferromagnetic. A Néel temperature of ~773°K was reported by Rosenqvist (*9*), whereas Holseth and Kjekshus (*8*) indicated a Néel temperature of about 1000°K. However, in later neutron diffraction studies of $FeSb_2$ by Holseth and Kjekshus (*10*), no magnetic ordering was found between 4.2°K and room temperature. It was concluded by Holseth and Kjekshus (*10*) that the anomalous behavior of the magnetic susceptibility was a result of the presence of impurities.

The purpose of the present investigation is to prepare well characterized single crystals of $FeAs_2$ and $FeSb_2$ by chemical vapor transport, and to ascertain the electrical and magnetic properties of pure compounds.

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* This work was supported by the United States Army Research Office, Durham, NC.

Experimental

Preparation

The single crystals of $FeAs_2$ and $FeSb_2$ used in this study were prepared by chemical vapor transport using chlorine as the transporting agent. The composition of the charge was a stoichiometric mixture (about 1.5 g) of freshly reduced iron and purified arsenic or antimony.[1] The amount of chlorine used in the reaction varied from 75 to 500 Torr. The charge zone and growth zone temperatures were 800 and 765°C for $FeAs_2$, and 700 and 650°C for $FeSb_2$. The transport reactions were carried out for 1–2 weeks. Crystals obtained by this method weighed up to 0.75 g and were 4–5 mm on an edge.

Analysis

The chemical analysis for Fe in $FeAs_2$ and $FeSb_2$ was based on the oxidation of Fe^{2+} by a standard solution of Ce^{4+}. The arsenic analysis was carried out by oxidizing the iron diarsenide in a solution of vanadium (V) sulfate to Fe^{3+} and As^{5+}, and back-titrating the reduced vanadium potentiometrically with standardized ceric sulfate. The arsenic content was calculated by difference. The composition obtained from the above analysis was $FeAs_{2.00\pm0.01}$. Antimony was determined electrolytically, and from the total iron and antimony content, the composition for the diantimonide was found to be $FeSb_{2.00\pm0.02}$.

In addition to the analyses by wet chemical methods, thermogravimetric analysis and X-ray diffraction were used to verify the stoichiometry of $FeAs_2$ and $FeSb_2$. The TGA apparatus consisted of a Cahn RG electro-balance, a vacuum system, a furnace, and a recorder. Approximately 50 mg of ground crystal was heated until a noticeable weight loss was observed. The samples were then X-rayed and the results showed that the cell parameters of $FeAs_2$ and $FeSb_2$ remained unchanged. In the $FeAs_2$ patterns FeAs lines were observed; there was also evidence for the presence of FeSb and Sb in the $FeSb_2$ samples.

Representative samples were analyzed by emission spectroscopy. The detectable impurities present in both compounds were magnesium 0.03–0.3 ppm, silicon <1 ppm, and copper <0.2 ppm. A single crystal of $FeAs_2$ was found to contain 8 ppm of chlorine as determined by neutron activation analysis (Gulf General Atomic Inc.).

Crystallography

Crystallographic parameters were determined on polycrystalline samples obtained by grinding representative sections of single crystals; silicon powder was added as an internal standard. A Norelco diffractometer with monochromatic radiation (AMR-202 focusing monochrometer) and a high intensity copper source ($\lambda_{(CuK\alpha_1)} = 1.5405$ Å) of focal spot 1.2×3.0 mm was used. In order to study the anisotropic behavior of the sample studied, crystals were oriented by means of the Laue back-reflection method.

Electrical Measurements

The electrical properties studied include the resistivity, Hall effect and Seebeck effect. Leads for the electrical measurements were attached to the crystal by an ultrasonic soldering technique with indium solder. If the samples were rectangular, resistivity measurements were made by a conventional 4-probe method. For samples having an irregular shape, the van der Pauw method (*16*) was used. Resistivity and Hall measurements were made in the manner described by Lee et al. (*17*).

Seebeck measurements were carried out at room temperature using copper-constantan thermocouples. An ice bath was used for the cold junction. The values obtained were corrected for the thermal emf of the copper wires used as leads to the samples. This correction was taken to be $+3.1$ μV/deg at room temperature. The Seebeck coefficients were reproducible from sample to sample.

Magnetic Measurements

Magnetic measurements were made on ground-up single crystals using a Faraday balance as described by Morris and Wold (*18*). The absence of a significant amount of ferromagnetic impurities (<1–2 ppm) for both compounds was verified by applying the Honda–Owen method (*18*, *19*). No corrections were made for core diamagnetism because of the large uncertainty in the magnitude of the correction.

Results

Crystallographic Measurements

The X-ray diffraction patterns were indexed on the basis of an orthorhombic unit cell. The

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[1] Spectroscopic grade Fe, As and Sb were obtained from Atomergic Chemetal Company, Division of Gallard–Schlesinger Chemical Corporation, New York.

TABLE I

Orthorhombic Unit Cell Dimensions of $FeAs_2$ and $FeSb_2$

Compound	*a*	*b*	*c*	Reference
$FeAs_2$	5.299 (1)	5.984 (1)	2.882 (1)	This work
	5.301 (1)	5.986 (1)	2.882 (1)	Holseth (14)
	5.301 (4)	5.979 (5)	2.882 (2)	Roseboom (20)
$FeSb_2$	5.829 (1)	6.535 (1)	3.196 (1)	This work
	5.833 (1)	6.52 (1)	3.19 (1)	Holseth (15)
	5.82	6.52	3.19	Hagg (21)

dimensions of the unit cells were in agreement with those reported by previous investigators (*14, 15, 20, 21*). The results are shown in Table I.

Electrical Measurements

The electrical resistivity of $FeAs_2$, measured as a function of temperature, is shown in Fig. 1. This material is an intrinsic semiconductor above 170°K; below this temperature impurity conduction is predominant. The thermal band gap calculated from the slope of the log ρ *vs* $10^3/T$ plot is 0.22 eV and the room temperature resistivity is 0.012 ohm cm. The log of the Hall coefficient of $FeAs_2$ *vs* $10^3/T$ is shown in Fig. 2. Above 170°K, the Hall coefficient is also proportional to an exponential function of temperature. For temperatures between 60–170°K, the Hall coefficient is almost constant. The Hall voltages are negative (*n*-type) over the entire measured temperature region. The Seebeck voltage at room temperature is ~ -200 μV/deg. This high value of the Seebeck coefficient confirms that $FeAs_2$ is a semiconductor, and the sign agrees with that obtained from Hall measurements.

The electrical properties of $FeSb_2$ were also studied as a function of temperature. The results of these measurements, shown in Figs. 3–5, indicate that $FeSb_2$ is a semiconductor with an extremely narrow band gap. As shown in Fig. 3, the impurity conduction was also observed for $FeSb_2$ below ~40°K. The activation energy is approximately the value of kT at room temperature. The resistivity at 300°K is 5×10^{-4} ohm cm and the resistivity ratio ($\rho_{300°K}/\rho_{10°K}$) is about 1000. Measurements on a single crystal along different directions showed anisotropic behavior. The results of these measurements from 77 to 300°K are given in Fig. 4. For the measurements made in the *ac* or *bc* planes, no change in slope was observed over the entire temperature range. However, for measurements made in the *ab* plane, a decrease in the slope was noted at temperatures above 100°K.

The Hall voltage of $FeSb_2$ was also found to be anisotropic. Samples measured with the *ab* plane perpendicular to the magnetic field (Fig. 5) showed *p*-type behavior over the whole temperature range. However, for samples having the *ac* or *bc* plane perpendicular to the magnetic field, the Hall coefficient was found to be *n*-type below ~100°K; at higher temperatures the measured voltage was too small for reproducible results. Although the smaller value of the Hall coefficient indicates that the number of charge carriers present in $FeSb_2$ is much larger than in $FeAs_2$, an exact calculation is not possible because two types of charge carriers are present. The

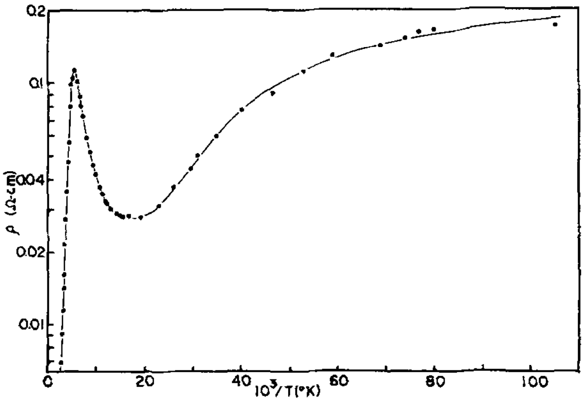

Fig. 1. Resistivity *vs.* Temperature for $FeAs_2$.

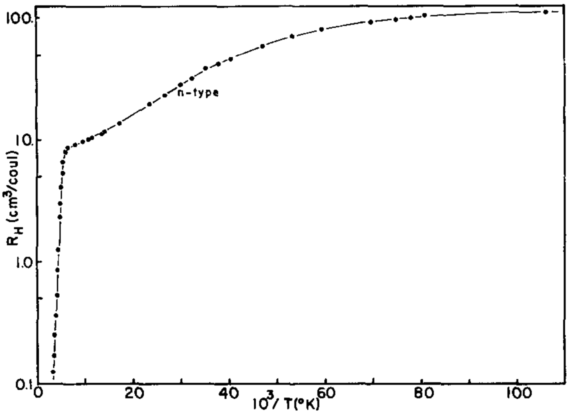

FIG. 2. Hall Coefficient *vs.* Temperature for $FeAs_2$.

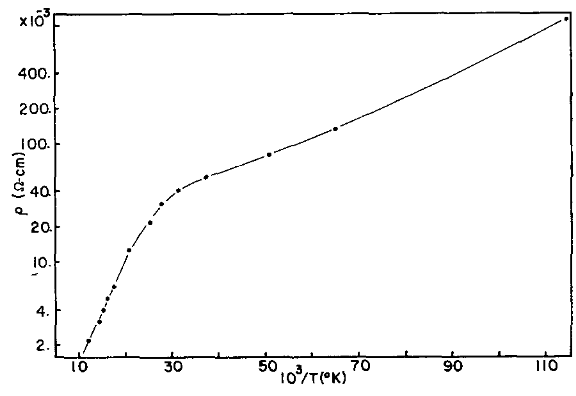

FIG. 3. Resistivity *vs.* Temperature for $FeSb_2$.

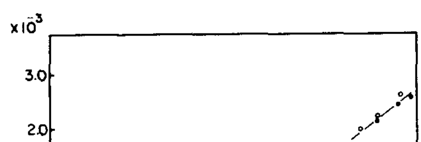

FIG. 4. Resistivity (Anisotropic) *vs.* Temperature for $FeSb_2$. ○ Measurement made in *ab* plane. ● Measurement made in *ac* or *bc* plane.

results of the Seebeck measurements are in agreement with those given by Johnston et al. (*6*). The value of the room temperature Seebeck coefficient is +30 $\mu V/°K$.

Magnetic Measurements

The magnetic properties of $FeAs_2$ and $FeSb_2$ were studied as a function of temperature. The results of these measurements are given in Fig. 6. $FeAs_2$ shows diamagnetic behavior with a molar susceptibility $\chi_M = -14.0 \times 10^{-6}$ emu/mole. For $FeSb_2$ it was found that the susceptibility increases as the temperature is increased from 80 up to 280°K. Above 280°K the susceptibility curve remains constant up to the decomposition temperature (573°K). The ratio of susceptibility $\chi_{300°K}/\chi_{77°K}$ is about 10 and the room temperature susceptibility is approximately 600 × 10^{-6}emu/mole.

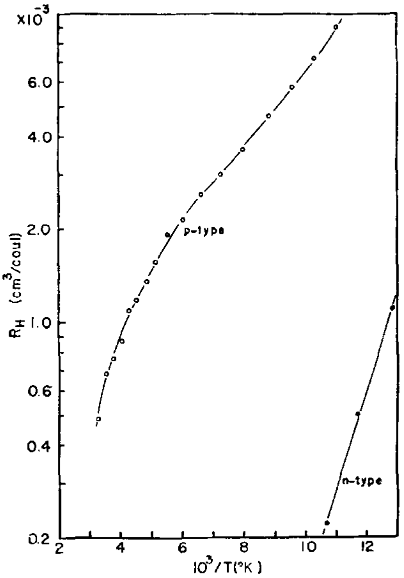

FIG. 5. Hall Coefficient *vs.* Temperature for $FeSb_2$. ○ Measurement made with the magnetic field ⊥ to the *ab* plane. ● Measurement made with the magnetic field ∥ to the *ab* plane.

Discussion

The thermal band gaps of $FeAs_2$ and $FeSb_2$ calculated from the resistivity are in agreement with those reported by Hulliger (*4*). As shown in Fig. 1, the resistivity curve of $FeAs_2$ below 170°K shows extrinsic behavior, i.e., resistivity increasing with increasing temperature. The resistivity reaches a maximum at about 170°K and in the intrinsic region above this temperature, the conduction process is dominated by the thermal excitation of electrons across the band gap; the activation energy is found to be 0.11 eV. The negative Hall coefficient of $FeAs_2$ indicates that electrons dominate the conduction process over the whole temperature range. Assuming that only one type of charge carrier is present (i.e., $R_H = -1/ne$), the carrier concentration between 60 and 170°K is almost constant and is $5 \times 10^{17}cc^{-1}$. The constant carrier concentration found in this region is probably a result of impurities, and the freezing out of these donor states is seen at lower temperatures. If each impurity atom donates one electron, the impurity concentration is calculated to be approximately 23 ppm; this is in good agreement with the results obtained from complete chemical analyses. The electrical measurements on $FeSb_2$ indicate that the band gap is much smaller than that of $FeAs_2$. Therefore, high conductivity is found for $FeSb_2$ as a result of the promotion of large numbers of carriers across the extremely narrow band gap. This is also supported by the small value of the Hall coefficient.

Magnetic measurements on $FeAs_2$ indicate diamagnetic behavior as proposed by previous investigators (*12*, *13*). However, this diamagnetic behavior has not been reported in any previous work. Instead, weakly temperature dependent paramagnetism was observed (*7*, *8*); this behavior was probably caused by impurities. For $FeSb_2$, the magnetic susceptibility increases with increasing temperature between 80 and 280°K. This is consistent with the results obtained by Holseth and Kjekshus (*8*). However, the antiferromagnetic behavior that they observed was not substantiated by neutron diffraction studies (*10*). Magnetic measurements made on pure, well crystallized single crystals indicate the absence of long range magnetic order. In addition, the thermogravimetric analyses and

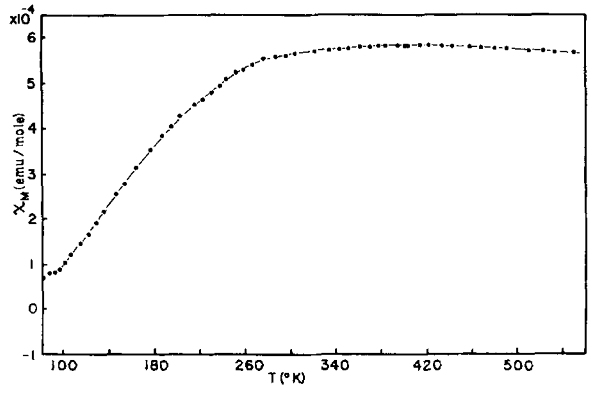

FIG. 6. Magnetic Susceptibility *vs.* Temperature for $FeSb_2$.

X-ray diffraction studies show that $FeSb_2$ decomposes into FeSb and Sb under vacuum at 573°K, and the magnetic data could not be reproduced after the sample was heated above this temperature.

The magnetic behavior shown for $FeSb_2$ in Fig. 6 is consistent with the narrow band gap obtained from the resistivity measurements. At very low temperatures the thermal energy is small compared to the band gap ($E_g > kT$). In this temperature region the electrons are in the d^4 low spin state, and $FeSb_2$ should be diamagnetic, as is $FeAs_2$. As the temperature is increased the thermal energy of the electrons increases and kT approaches the value of E_g (i.e., $E_g = kT$). This may be accounted for by a partial unpairing of the 3-d electrons due to promotion to the conduction band. The unpairing of the 3-d electrons is consistent with an increase in susceptibility as the temperature is increased, as was observed in the temperature region from 80 to 280°K. In the temperature region above 280°K, kT becomes larger than the band gap, and van Vleck temperature independent paramagnetism is observed (*22*).

Below liquid nitrogen temperature, $FeAs_2$ and $FeSb_2$ show similar magnetic properties. The differences observed in the magnetic properties of $FeAs_2$ and $FeSb_2$ above 77°K can be explained by a one-electron energy scheme proposed by Goodenough (*23*). The scheme proposed by Brostigen and Kjekshus (*13*) is similar, but their rationale for splitting of the t_{2g} bands is questionable. The marcasite structure is shown in Fig. 7. The metal atoms are surrounded by a distorted octahedral environment of anions. Each anion occupies a distorted tetrahedral site and is surrounded by one anion and three cations. The metal–anion–metal angle represented by α in Fig. 7 is approximately 72.5° for $FeAs_2$ rather than 109° as expected for an ideal tetrahedral configuration. The C_{2h} symmetry of the cation site gives rise to splitting of the 3-*d* orbitals as shown in Fig. 8. The σ_M bonding and σ^*_M antibonding bonds are formed by the interaction of anion–anion pairs; the M–X bonding (σ) and corresponding antibonding (σ^*) bands are formed as the result of overlap between the metal σ bonding orbitals and the three remaining sp^3 hybrid orbitals per anion. However, the lack of tetrahedral angles, particularly the angle $\alpha \cong 72.5°$ (for $FeAs_2$) in Fig. 7, indicates not only a deviation from ideal sp^3 hybridization, but also the existence of important bonding with the d orbitals directed along the c axis, which we label $a_\parallel$ in Fig. 8. Since the 3-d orbitals are antibonding with respect to the anion array, covalent mixing destabilizes the $a_\parallel$ orbitals relative to the b orbitals. This relative destabilization is larger the smaller the angle α. In the marcasite form of FeS_2, the angle $\alpha \cong 97°$ suggests probable overlapping of the filled $a_\parallel$ and b bands. Given filled $a_\parallel$ orbitals, no stabilization can be achieved by covalent bonding. Thus, Goodenough (*23*) argues that the short *c* axis in $FeAs_2$ as compared to FeS_2 is due to cation–anion bonding, not to cation–cation repulsions as suggested by Brostigen and Kjekshus (*13*). For the compounds $FeAs_2$ and $FeSb_2$, there are 18 valence electrons per formula unit (Fe contributes 8 electrons

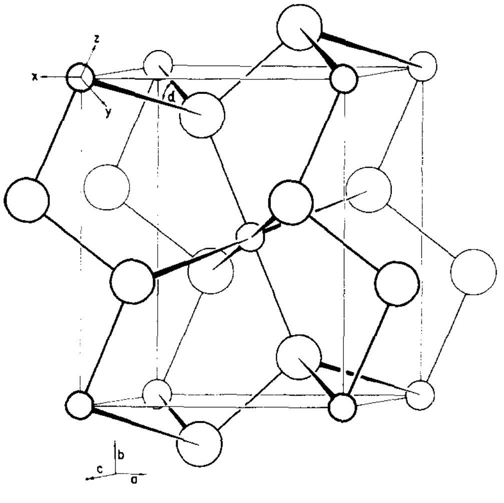

FIG. 7. The Orthorhombic Marcasite Structure.

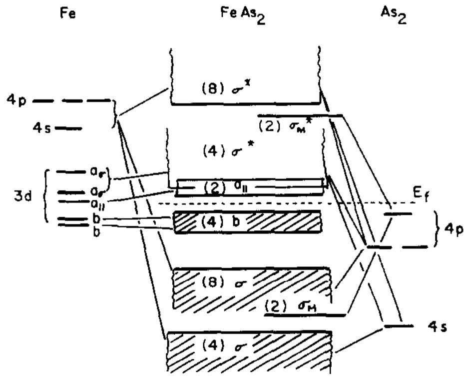

FIG. 8. One-Electron Energy Levels for Outer Electrons of $FeAs_2$ with the Marcasite Structure.

and 5 electrons are contributed from each As or Sb atom). Fourteen electrons per molecule (two electrons per σ_M bond and 12 electrons in M–X σ bands) are required to fill up the bonding orbitals. Therefore, there remain 4 electrons per molecule. It can be seen from Fig. 8 that the diamagnetic, semiconducting properties of $FeAs_2$ and $FeSb_2$ may be naturally understood if the $a_{\parallel}$ band lies above the b bands. Then, for the case of low-spin $FeAs_2$ at low temperature, the lower b band is completely filled and the upper $a_{\parallel}$ band is empty. This scheme requires an energy separation of approximately 0.22eV (measured band gap) between the $a_{\parallel}$ and b bands. Brostigen and Kjekshus (*13*) suggested that such a splitting of the t_{2g} bands as shown in Fig. 8 resulted from metal–metal repulsions along the c axis. However, as pointed out by Goodenough (*23*), such a repulsion would simply broaden the t_{2g} band without splitting it, so long as the cations remain equally spaced along the c axis. It seems more reasonable to assume with Goodenough (*23*) that the $a_{\parallel}$ orbitals have been destabilized by covalent bonding with anions.

Although the temperature coefficient of the resistivity of $FeSb_2$ has the sign of a semiconductor any energy gap must be extremely small. Even at liquid nitrogen temperature, there seem to be enough electrons promoted into the $a_{\parallel}$ conduction band to give a paramagnetic, rather than a diamagnetic susceptibility. The fact that $FeSb_2$ thus appears to be more like a semimetal than a semiconductor is consistent with a larger angle $\alpha \cong 76°$ in $FeSb_2$ than in $FeAs_2$. In addition, $FeSb_2$ is more covalent than $FeAs_2$ because of the larger, more polarizable anion; therefore, the $a_{\parallel}$ and b bands formed by the 3-d orbitals will be broader, thus narrowing the band gap further. As the temperature is increased from 77°K, the thermal energy is sufficient to promote relatively large numbers of electrons into the $a_{\parallel}$ band, and the $a_{\parallel}$ band would tend to become relatively more stable. The thermal distribution of the 3-d electrons, therefore, may give rise to the anomalous increase in the paramagnetic moment of $FeSb_2$ as the temperature is increased. The semiconductor $FeAs_2$, on the other hand, remains diamagnetic throughout the entire temperature region studied.

Further support for this explanation is also found in the Mössbauer studies of these compounds (*24*, *25*). A slight decrease was noted in the isomer shift of both $FeAs_2$ and $FeSb_2$ as the temperature was increased; and only for $FeSb_2$ was a significant decrease in the quadrupole splitting observed with increasing temperature. The decrease in the isomer shift is due to the second order Doppler effect and does not require any change in the 3-s and 3-d electron density around the Fe nucleus as a function of temperature. However, the decrease in the quadrupole splitting, observed for $FeSb_2$, requires a change in the electric field gradient. Such a change can be accounted for by considering the thermal distribution of the electrons among the 3-d bands that is consistent with the magnetic and electrical measurements. The details of the Mössbauer study are presented in the following paper (*25*).

Acknowledgments

The authors wish to thank Mr. H. H. Whitaker of R.C.A. Laboratories at Princeton, N.J., for the emission spectrographic analyses, and Dr. W. W. Russell of Brown University for advice concerning the chemical analyses. In addition, they would like to thank Dr. J. B. Goodenough at M.I.T., Lincoln Laboratories, for helpful discussions.

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