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Mössbauer Spectra, Magnetic and Electrical Behavior of $Ba_{1+x}Fe_2S_4$ Phases

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The Mössbauer spectra, and magnetic and electrical properties of $Ba_{1+x}Fe_2S_4$ infinitely adaptive phases with $0.074 \leq x \leq 0.142$ and of $BaFe_2S_4$ were studied. The properties are highly anisotropic because of the presence in the structure of one-dimensional infinite chains of edge sharing FeS_4 tetrahedra. $BaFe_2S_4$ is a semiconductor, $E_g = 0.66$ eV; magnetic susceptibility can be fit by a one-dimensional Heisenberg model with spin 5/2 and $J/k = -30°K$. The $Ba_{1+x}Fe_2S_4$ phases have Curie–Weiss behavior with an effective moment of about 2 B.M. The moment increases with x. These phases are metallic. The Mössbauer isomer shift varies linearly with valence, increasing with increasing x. The single quadrupole split absorption line characteristic of these compounds disappears at about 270°K and a complex spectrum consisting of overlapping hyperfine patterns appears at lower temperatures. Magnetic short-range ordering is responsible for this behavior although the susceptibility in this temperature range does not reflect this effect.

Introduction

In order to study the interrelationships between the structure and physical properties of the $Ba_{1+x}Fe_2S_4$ series and to gain some insight into the dimensionality of this system the Mössbauer spectrum, the electrical conductivity, and the magnetic susceptibility were investigated for compounds in which values of x were zero and nonzero. We have shown that the infinitely adaptive series $Ba_{1+x}Fe_2S_4$ exists for $0.072 \leq x \leq 0.142$ and that $BaFe_2S_4$ is not a member of this series (*1*). It is reasonable to expect that the physical properties of the members of the series are very similar, at most showing subtle variations with composition, but the $x = 0$ compound may have a quite different behavior. Previous results have indicated that when $x > 0$ the phases contain delocalized electrons with consequent effects on electrical resistivity (*2*). The physical properties for these compounds must also be highly anisotropic because the FeS_4 tetrahedra share two opposite edges to create infinite one-dimensional chains which are separated laterally by about 6 Å. Within the chain the Fe–Fe distances are about 2.7 Å and permit direct overlap of the iron d orbitals (*1, 3, 4*). Physical properties, such as electrical conductivity, will be strongly affected by the directionality of the transition metal interactions and the results from these measurements should contribute toward an understanding of the physical behavior of low dimensional solids.

Experimental

Mössbauer spectra were obtained with an Austin Science Associates Mössbauer

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spectrometer drive instrument model 53, with a range of 0–60 cm/sec operated in the time mode. Data were accumulated in a Southwest Technical Products model 6800 minicomputer. The source was 20 mC of ^{57}Co diffused into palladium foil and used at room temperature. Velocity calibration was obtained using a laser interferometer. The absorbers consisted of a finely ground powder of approximately 150 mg/in.^{2} thickness. The data were corrected for parabolic motion effects, and the spectra were fit by least-squares analysis assuming Lorentzian line shapes. A value of 0.218 mm/sec was added to each line position to correct for source line shift due to the palladium matrix and to reference the spectra to metallic iron. The reproducibility of the line positions is generally within 1% or better. Low temperature spectra were obtained using an Air Products Displex Model CS-202 closed cycle refrigeration system. Temperature control of the system was accomplished by comparing the output voltage of a calibrated silicon diode to a reference voltage.

A Faraday type magnetic balance was used to measure the susceptibilities of the $Ba_{1+x}Fe_2S_4$ phases.

A two probe technique was used for resistance measurements because of the small size of the crystals. The apparatus consisted of a Displex Model CS-202 closed cycle refrigeration system with two spring loaded probes mounted on the low temperature tip of the refrigerator. Temperature control of $\pm 0.1°K$ was obtained by use of a controller which monitored the output of a thermocouple mounted on the cold tip and varied the power to a resistance heater wound around the cold tip. A minimum temperature of approximately 20°K was obtainable at a pressure of 90 μm in the sample chamber. Two different sample preparation techniques were used for measurements on single crystals and single crystal bundles. The bundles were held in place by the force of the probes and good contact was ensured by applying silver paint to the contact points. When single crystals were used, they were glued to a glass slide, masked with a small strip of tape, and shadowed with gold in a vacuum evaporator. In this procedure the crystal forms a conducting bridge of known dimensions between the two gold contacts. The glass slide was placed in the refrigerator and held in place by probes on the gold contacts. Silver paint was applied to ensure good contacts. In order to check for ohmic contacts, the I–V characteristics of the sample were obtained using a curve tracer. Both positive and negative polarities had to show identical results before measurements were taken. A Keithley 602 electrometer was connected to the probes and resistance measurements were obtained from room temperature to approximately 30°K in about 10°K temperature intervals and at least 10 min equilibration intervals were used at each temperature setting.

It is essential that single phase materials be available for these measurements and we used the phase diagram information to prepare each compound studied. The purity was judged on the basis of powder X-ray diffraction results (*5*, *1*). The 10*p*, 21*q*, and 21*p* diffraction lines are very sensitive indicators of the presence of other phases because they will assume asymmetric shapes. It is estimated that less than 5% of an admixed phase will produce such asymmetry. The Mössbauer spectrum is also very sensitive to the presence of a second phase and when both criteria yielded indications of single phase compounds, they were subsequently used in the other measurements.

Results

Mössbauer Spectroscopy

The dependence of Mössbauer isomer shift on the valence of iron tetrahedrally coordinated to sulfur can be expressed by a linear relationship to valence, $\delta = 1.40 - 0.4V$ (*6*). For x Ba^{2+} ions in the series $Ba_{1+x}Fe_2S_4$, $2x$ Fe^{3+} ions must be reduced to Fe^{2+} so that the average iron valence becomes $V = 3 - x$ leading to the relationship between I.S. and x, $\delta = 0.20 + 0.40x$. The room temperature Mössbauer spectra from 12 $Ba_{1+x}Fe_2S_4$ compounds with $0.083 \leq x \leq 0.132$ and from $BaFe_2S_4$ exhibit a single quadrupole split absorption line indicating that the crystallographically distinct Fe can be considered to display a single average valence value (*2*). The observed and calculated isomer shifts for these 12 compounds are shown in Table I with excellent agreement between observed and calculated values when $x \geq 0.1$.

TABLE I

ROOM TEMPERATURE ISOMER SHIFTS WITH RESPECT TO METALLIC Fe FOR MEMBERS OF THE INFINITELY ADAPTIVE SERIES $Ba_{1+x}Fe_2S_4$ AND FOR $BaFe_2S_4$; CALCULATED FROM $\delta = 0.20 + 0.4x$

x	δ_{obs} (mm/sec)	δ_{calc} (mm/sec)
0.083	0.223	0.233
0.086	0.221	0.234
0.089	0.222	0.236
0.089	0.225	
0.092	0.227	0.237
0.106	0.241	0.242
0.112	0.244	0.245
0.115	0.251	0.246
0.127	0.248	0.251
0.127	0.254	
0.132	0.256	0.253
0.132	0.257	
0.000	0.182	0.200

The low temperature Mössbauer behavior of the 12 phases $Ba_{1+x}Fe_2S_4$ $0.083 \leq x \leq 0.132$ is complicated. As the temperature is lowered from room temperature, the two absorption lines weaken and then vanish into the background at a temperature between 260 and 283°K (Figs. 1a and b) depending on the value of x; the effect is observed at higher temperatures for higher values of x. As the temperature is lowered further, a poorly resolved, multiline spectrum is obtained at 195°K. In Fig. 2 is shown the spectrum obtained at 78°K for $Ba_{1.089}Fe_2S_4$ and it compares favorably with that published by Reiff *et al.* (*2*). This rather weak absorption spectrum contains at least two and possibly more overlapped hyperfine patterns. This type of spectrum could be due to magnetic ordering which begins near 273°K. The magnetic measurements (*v.i.*) are consistent with such a postulate. Stephenson has pointed out that a one-dimensional Ising chain with nearest and next-nearest neighbor interactions may exhibit an abrupt change in short range order at a particular temperature while the magnetic susceptibility over this region has a smooth temperature dependence (*7*). He suggests that this disorder point, T_d, may be observed by neutron diffraction (*8*). The present results indicate that this type of ordering could be observed experimentally through the use of Mössbauer spectroscopy.

A crystallographic phase transition near 273°K could cause such behavior. We carried out low temperature X-ray diffraction experiments down to 144°K on powders and on a single crystal and saw no evidence for such a transition. If localization of the *d* electrons took place so that Fe^{3+} and Fe^{2+} become distinguishable, i.e., a Verwey transition, the Mössbauer spectrum should display two hyperfine patterns whose areas should be in the ratio of Fe^{3+}/Fe^{2+} for a given value of x. The observed hyperfine patterns have approximately equal intensities. Furthermore, this low temperature pattern exists also for the $x = 0$ phase where only Fe^{3+} is present. The electrical conductivities for $Ba_{1+x}Fe_2S_4$ also show that no localization of electrons occurs (*v.i.*). The possibility that relaxation effects (*9, 10*) may be responsible for these observations can be ruled out because these usu-

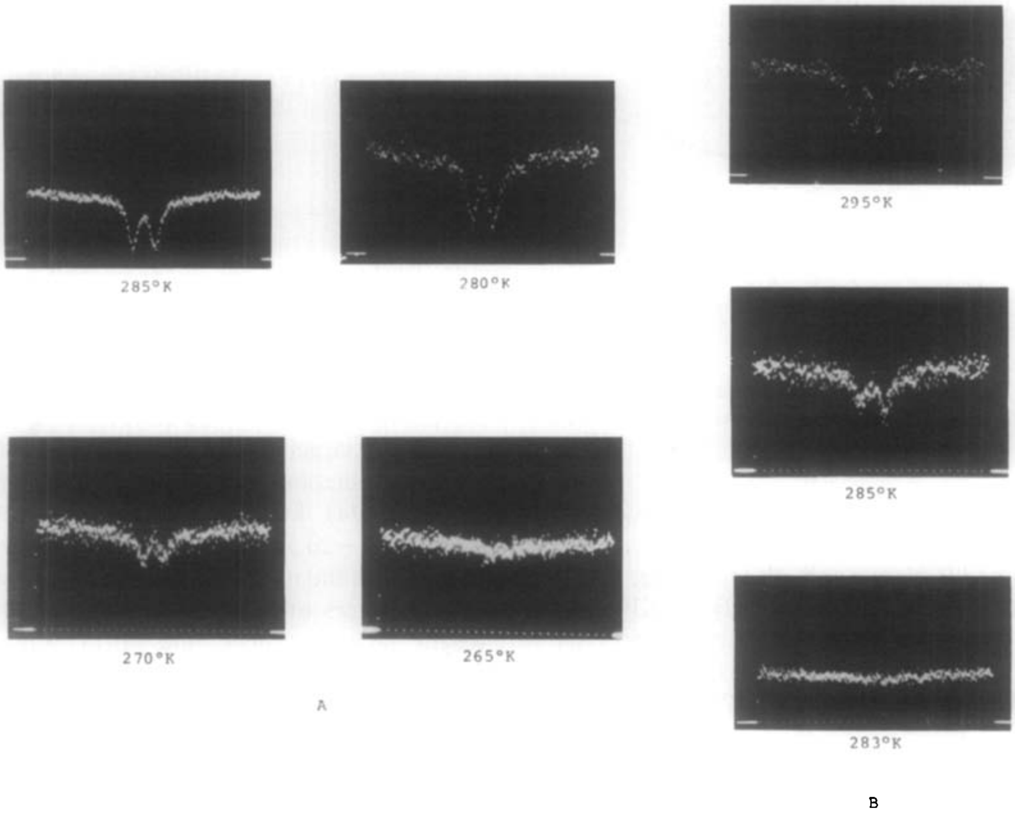

FIG. 1. Mössbauer spectra at various temperatures for (a) $BaFe_2S_4$ and (b) $Ba_{1.089}Fe_2S_4$.

ally are observed below 30°K. Short range magnetic ordering is the most likely explanation for the temperature dependence of the Mössbauer spectra.

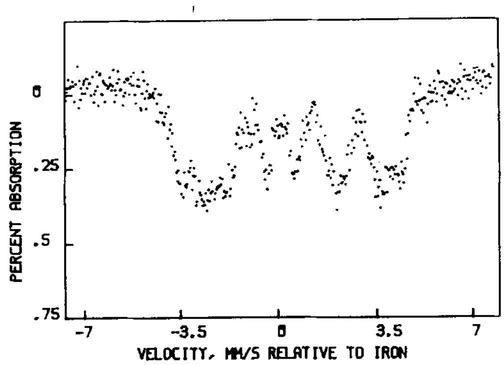

FIG. 2. Mössbauer spectrum for $Ba_{1.089}Fe_2S_4$ at 78°K.

Magnetic Susceptibility

$BaFe_2S_4$. The susceptibility of $BaFe_2S_4$ (Fig. 3) varies slowly over the temperature

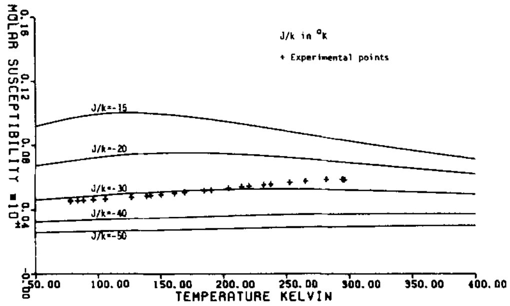

FIG. 3. Comparison between the experimental values of susceptibility for $BaFe_2S_4$ (+) and calculated values from a 5/2 spin Heisenberg model for various J/k values.

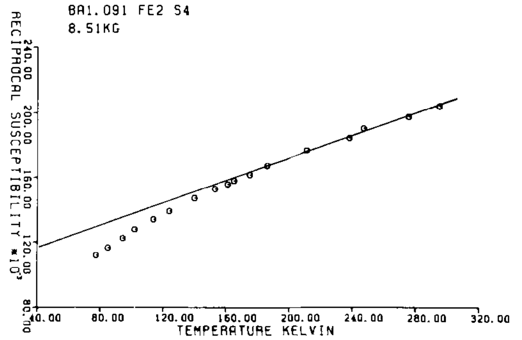

FIG. 4. Plot of $1/\chi$ vs T for $Ba_{1.091}Fe_2S_4$. The linear portion of the curve yields μ_{eff} = 2.07 B.M. and θ = −265°K.

range 77°K to room temperature and does not display a Curie–Weiss type dependence on T. It increases with increasing temperature and behaves similarly to $KFeS_2$ (*11*). The behavior of the molar susceptibility vs T was fit to the expression obtained by Wagner and Friedberg (*12*) for a classical $S = 5/2$ Heisenberg Hamiltonian and follows the curve for J/k = −30°K. The coupling constant is larger than that reported for the linear antiferromagnets Ba_2MnS_3 (*13*) and Ba_2FeS_3 (*14*) for which the values are −12.3 and −20.5°K, respectively. In these compounds the magnetic atoms are located at the centers of MnS_4 or FeS_4 tetrahedra which share corners and form infinite chains. The exchange energy results primarily from superexchange via the inter-

TABLE II

VALUES OF μ_{eff}, θ, AND Fe–Fe DISTANCES VS COMPOSITION FOR $Ba_{1+x}Fe_2S_4$

x	μ_{eff} (B.M.)	Fe–Fe (Å)
0.074	1.93	2.72
0.091	2.07	2.74
0.133	2.35	2.78

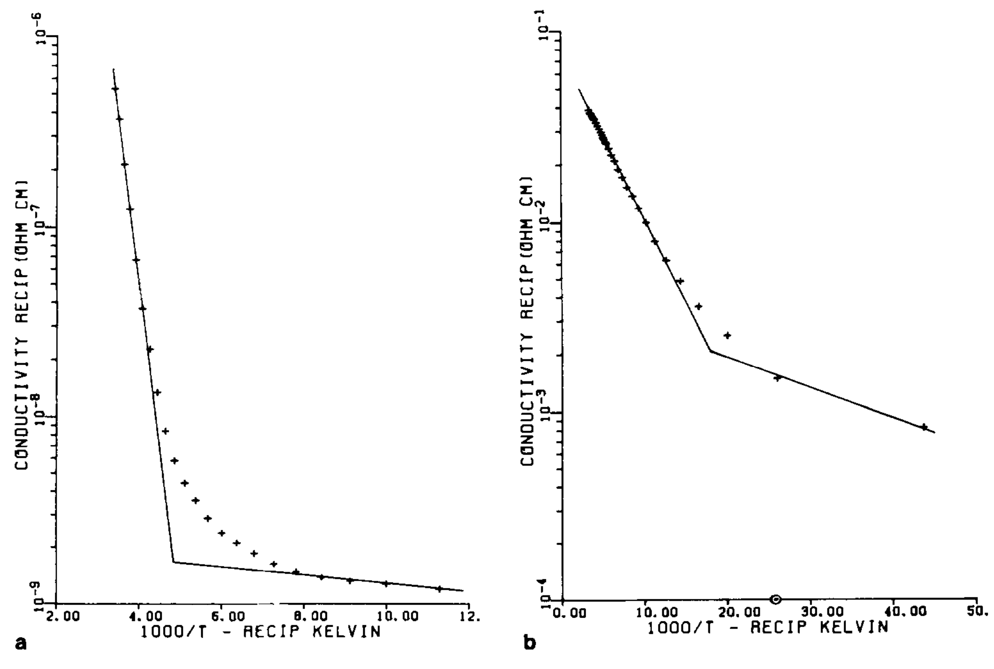

FIG. 5. ln σ vs $1/T$ for (a) $BaFe_2S_4$ and (b) $Ba_{1.086}Fe_2S_4$ single crystal. The activation energy E_a = 0.017 eV.

vening sulfur atoms as the metal–metal separation >4 Å prohibits direct exchange. Thus the magnetic behavior of Ba_2MnS_3 and Ba_2FeS_3 follows a Curie–Weiss law while this is not the case for $BaFe_2S_4$ and $KFeS_2$. In the latter two compounds tetrahedra share edges and the Fe–Fe separation is 2.7 Å, giving rise to antiferromagnetic superexchange between α-spin electrons of Fe^{3+} (*4*). The infinite chain of edge sharing tetrahedra creates a *d* band which is filled by the α-spin electrons and an empty b_{1g} band. For this ground state no effective magnetic moment should be observed. The weak moment which is seen for both $BaFe_2S_4$ and $KFeS_2$ can be explained as due to electrostatic repulsion between the α-spin electrons causing a residual localized moment on Fe^{3+}.

$Ba_{1+x}Fe_2S_4$. The room temperature susceptibility of the $x \neq 0$ phases varies little with the value of x and is about 5×10^{-6} emu/g, or about 1/6 of the susceptibility observed in the $x = 0$ phase. The most striking difference between the $x = 0$ and $x \neq 0$ susceptibilities is that the latter have a Curie–Weiss temperature dependence. A plot of $1/\chi_g$ vs T (Fig. 4) for $x = 0.091$ ($x = 0.074$ and 0.133 show similar behavior) shows a linear region above about 140°K and incipient ferrimagnetic ordering at this temperature. The effective magnetic moment calculated from the linear portion is 2.07 B.M. and $\theta = -265$°K. Assuming a spin only contribution to moment, the effective moment is indicative of slightly more than one spin per iron atom in the formula $Ba_{1.091}Fe_2S_4$. The introduction of excess barium ions requires that twice the number of ferric ions be formally reduced to ferrous to maintain charge neutrality. This $d^{6\beta\text{-spin}}$ electron occupies the b_{1g} band (*4*). The expected effective spin only moment for one electron is 1.73 B.M. It is postulated that the introduction of electrons into this previously empty band causes increased polarization effects near the iron centers so that the total moment is larger than for just one unpaired spin. In Table II are shown the various values of μ_{eff}, θ, and Fe–Fe distances vs composition. The increasing Fe–Fe distance with increasing x will decrease the value of the overlap integral and increase the polarization effect. These effects are reflected in the decreasing values of θ and increasing values of μ_{eff}.

Electrical Properties

One of the properties which best characterizes linear chain materials is the temperature dependence of the electrical conductivity. In general three classes of temperature-dependent conductivity behavior have been categorized by Epstein and Miller (*15*).

The resistance of a single crystal with composition $Ba_{1.086}Fe_2S_4$ and several single crystal "bundles" having good parallel alignment where measured parallel to the *c* axis. The single crystal was 0.082 cm long × 0.032 cm thick with a square cross-section and typical bundles were approximately 0.25 cm long with a cross-sectional area of approximately 0.014 cm².

The experimental conductivities vary smoothly with temperature for both $x = 0$ and $x \neq 0$ phases and plots of $\ln \sigma$ vs $1000/T$ are shown in Fig. 5 for $BaFe_2S_4$ and for a single crystal of $Ba_{1.086}Fe_2S_4$. The high temperature linear region for $BaFe_2S_4$ yields a value for $E_g = 0.66$ eV while the activation energies for $Ba_{1+x}Fe_2S_4$ vary between 0.017 and 0.065 eV. The room temperature conductivity of $BaFe_2S_4$ is approximately 5×10^{-7} ohm^{-1} cm^{-1} while that of the $x \neq 0$ compounds is about 0.1 ohm^{-1} cm^{-1} for the single crystal bundles and about 0.03 ohm^{-1} cm^{-1} for the $x = 0.086$ single crystal. The semiconducting behavior of $BaFe_2S_4$ and the nearly metallic values of conductivity for the $Ba_{1+x}Fe_2S_4$ phases can be accounted for by the same band structure which was used to explain

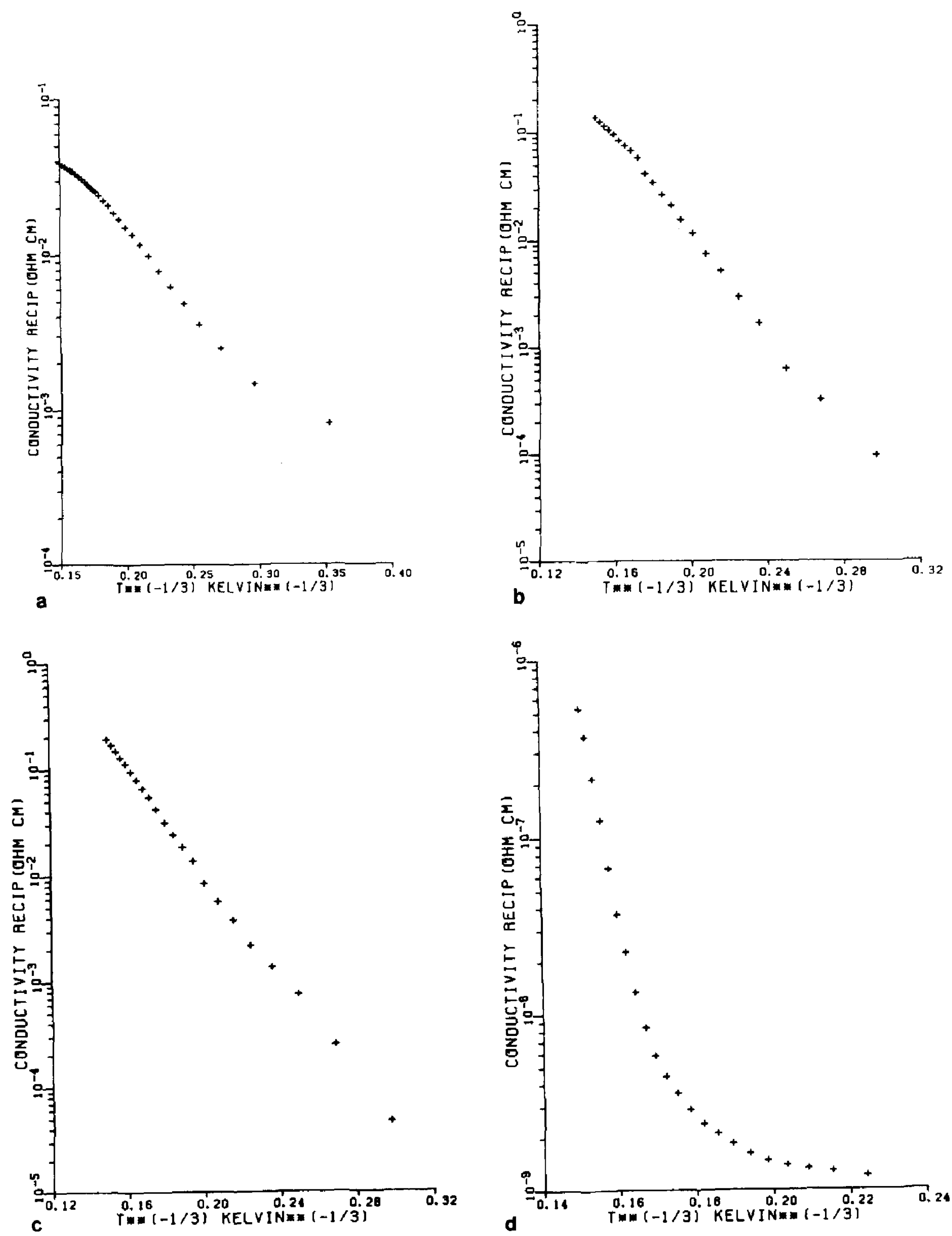

FIG. 6. Plots of ln σ vs $T^{-1/3}$ for (a) $Ba_{1.086}Fe_2S_4$; (b) $Ba_{1.096}Fe_2S_4$; (c) $Ba_{1.112}Fe_2S_4$; (d) $BaFe_2S_4$.

the magnetic properties. In $BaFe_2S_4$ the antiferromagnetic exchange gives rise to a filled band populated by the α-spin electrons and an empty b_{1g} band and typical semiconductor behavior is observed. The introduction of additional electrons in the

$Ba_{1+x}Fe_2S_4$ compositions places them into the previously empty b_{1g} band and gives rise to metallic behavior. The continuous variation of the conductivity at low temperatures and the very low values of activation energies can be explained by Zeller's interrupted strand model for one-dimensional chains (*16*). In this model the conductivity is governed by impurities and imperfections in one-dimensional chains, and conduction is limited by the ability of electrons to hop from one chain to another. This process leads to no single activation energy but to a range of activation energies and to a log $\sigma \propto T^{-\mu}$, $1/3 \leq \mu \leq 1/2$, dependence. The linear relationship shown when ln σ vs $T^{-\mu}$ for $\mu = 1/3$, is plotted, for the $Ba_{1+x}Fe_2S_4$ data (Fig. 6) lends strong support to such an interrupted chain model conduction mechanism. The model does not fit the low temperature conductivities of the $x = 0$ phase, as would be expected on the basis of the postulated band structure.

Conclusion

The crystal structures of the compounds represented by the formula $Ba_{1+x}Fe_2S_4$ consist of linear chains formed by edge sharing FeS_4 tetrahedra. The intrachain Fe–Fe distances are 2.6–2.7 Å while interchain distances are about 6 Å. The close Fe–Fe distances permit antiferromagnetic exchange and produce a filled band from the α-spin electrons. The β-spin electrons, when present, populate the b_{1g} band. In $BaFe_2S_4$ no β-spin electrons are present and the magnetic and electrical behavior are consistent with that of a semiconductor. As additional electrons are added in the formation of the $Ba_{1+x}Fe_2S_4$ phases, β-spin electrons begin to populate the previously empty b_{1g} band. These compounds are metals and the magnetic and electrical observations are consistent with this type of behavior. The room temperature Mössbauer isomer shifts show a linear relationship with the iron valence. The quadrupole split absorption doublet vanishes at about 270°K and a complex spectrum containing at least two overlapped hyperfine patterns forms at lower temperatures. This behavior is most likely due to the onset of magnetic ordering at about 270°K.

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