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# Studies on the Compounds in the Ba–Fe–S System. I. Linear Chain Antiferromagnetism of $Ba_2FeS_3$ and Related Compounds $Ba_2CoS_3$ and $Ba_2MnS_3$

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Magnetic susceptibilities of $Ba_2FeS_3$, $Ba_2CoS_3$, and $Ba_2MnS_3$ show rounded maxima at 130, 125, and 100 K, respectively, which are due to quasi-one-dimensional antiferromagnetic short-range ordering. Intrachain interactions, $J/k$, are estimated to be $-20$, $-15$, and $-12$ K, respectively. $^{57}Fe$ Mössbauer spectra of $Ba_2FeS_3$ and $^{57}Fe$-doped $Ba_2CoS_3$ and $Ba_2MnS_3$ at 4.2 K show long-range antiferromagnetic ordering, due to the interchain interaction. The profile of Mössbauer spectra at 4.2 K is analyzed based on the coexistence of magnetic hyperfine and quadrupole interactions, and magnetic hyperfine fields at 4.2 K are estimated to be 36, 29, and 59 kOe, respectively.

## Introduction

In recent years, many compounds with various compositions and crystal structures in the ternary Ba–Fe–S system have been reported by Steinfink and collaborators (*1*–*3*). In some of these compounds, iron ions are tetrahedrally coordinated by sulfur ions and the $FeS_4$ tetrahedra link by edge and/or corner sharing into infinite chains. $Ba_2FeS_3$, one of these compounds, is isostructural with $K_2CuCl_3$; space group *Pnma* with $Z = 4$ (*1*). $FeS_4$ tetrahedra in $Ba_2FeS_3$ (slightly distorted with approximately $C_{2v}$ symmetry) make an infinite linear chain by corner sharing along the $b$-axis. Barium ions occupy sites among the chains coordinated by six sulfur ions (trigonal prism type). The iron–iron distance along the chains is 4.25 Å via $S^{2-}$ ions whereas between chains it is 6.09 Å via $Ba^{2+}$ ions. The chemical bonding within the chain (Fe–S bond) may seem to have more covalent character compared with the bonding between chains (Ba–S bond).

The structure features suggest a linear chain magnetic interaction in this compound. Previous measurements of some physical properties reported in the literature (*4*, *5*) were performed only in the temperature range above 78 K and the results are summarized as follows. A maximum in the $\chi$–$T$ curve at about 110 K was observed but the $^{57}Fe$ Mössbauer spectrum at 78 K showed no magnetic splitting. Electrically, $Ba_2FeS_3$ is a highly resistive semiconductor

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($\rho_{300\,\mathrm{K}} = 10^{+4}\ \Omega \cdot \mathrm{cm}$, $E_a = 0.60$ eV), which suggests that electrons around $Fe^{2+}$ ions are localized (*3*, *4*). In order to obtain further understanding of magnetic interaction and ordering in this compound, measurements at lower temperatures are needed. We report here the results of magnetic susceptibility and Mössbauer measurements for $Ba_2FeS_3$ in the temperature range from 4.2 to 300 K.

Related linear chain compounds $Ba_2CoS_3$ (*1*) and $Ba_2MnS_3$ (*6*), having a crystal structure very similar to that of $Ba_2FeS_3$, were also reported. $Ba_2CoS_3$ ($K_2CuCl_3$ type) is isostructural with $Ba_2FeS_3$, while $Ba_2MnS_3$ ($K_2AgI_3$ type) is not exactly isostructural with $Ba_2FeS_3$. The difference between these two structures is in the stacking of tetrahedron chains in the *b*-plane (*7*). In the case of $Ba_2MnS_3$, Grey and Steinfink (*6*) measured its magnetic susceptibility above 50 K and pointed out the linear chain magnetic character. We also measured magnetic susceptibility down to 4.2 K and $^{57}Fe$ Mössbauer spectra of $^{57}Fe$-doped samples for $Ba_2CoS_3$ and $Ba_2MnS_3$ in order to investigate their magnetic properties and to compare them with the results for $Ba_2FeS_3$.

## Experimental

Samples were prepared by a method similar to that described in the literature (*1*, *6*): reaction of BaS, metal (Fe, Co, Mn), and S in evacuated silica tubes at 1000°C. The charges were enclosed in graphite crucibles in order to avoid reaction with silica. Annealing at 1000°C for 2 weeks was needed to obtain single-phase materials. For Mössbauer measurements, 2 atom% $^{57}Fe$-doped samples of $Ba_2CoS_3$ and $Ba_2MnS_3$ were prepared. Magnetic susceptibility was measured using a magnetic torsion balance in the temperature range from 4.2 to 300 K. $^{57}Fe$ Mössbauer spectra were obtained using a constant acceleration drive operated in the time mode. The source was $^{57}Co$ diffused into copper foil. Measurements were performed at 4.2 K, 77 K, and room temperature. Relative velocity was calibrated by the spectrum of α-Fe at room temperature.

## Results and Discussion

### 1. Magnetic Susceptibility

Temperature dependence of the magnetic susceptibility for $Ba_2FeS_3$, $Ba_2CoS_3$, and $Ba_2MnS_3$ in the temperature range from 4.2 to 300 K is shown in Fig. 1. The features of the susceptibility curves are similar among these three compounds. Rounded maxima at 130, 125, and 100 K, respectively, are observed, which are typical of quasi-one-dimensional antiferromagnets. Even above these maxima up to 300 K, the χ–*T* relations are not exactly Curie–Weiss type, probably due to residual intrachain short-range interaction within a chain. These results for $Ba_2FeS_3$ and $Ba_2MnS_3$ agree with previous measurements (*5*, *6*). In the lower temperature region, χ–*T* curves do not

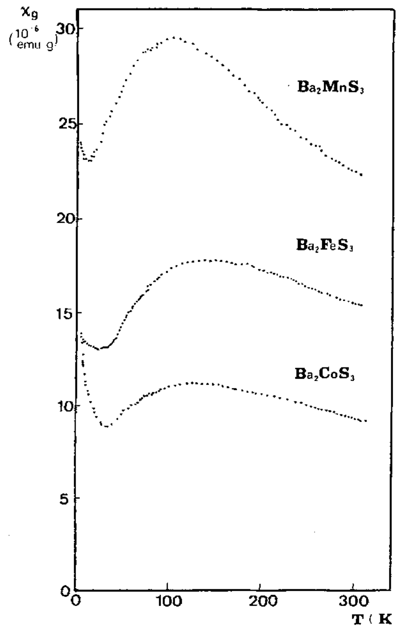

FIG. 1. Temperature dependences of gram magnetic susceptibility of $Ba_2MS_3$ (*M* = Fe, Co, Mn).

show any sharp anomalies indicating the onset of long-range magnetic ordering, but an increase of $\chi$ was observed.

One-dimensional magnetic systems have been investigated from many theoretical and experimental aspects (*8*, *9*). Typical experimental features of linear chain antiferromagnets are broad maxima in $\chi$–$T$ and $C_v$–$T$ curves due to short-range antiferromagnetic ordering within the chain. We intended to fit the above results to the theoretical $\chi$–$T$ curve. Judging from the electron configuration of magnetic ions, it is suggested that $Fe^{2+}$ [$d^6$] and $Co^{2+}$ [$d^7$] have anisotropic electronic structures and that $Mn^{2+}$ [$d^5$] has an isotropic electronic structure. In the case of $Ba_2MnS_3$, Grey and Steinfink reported a fit to theoretical $\chi$–$T$ curves based on the Heisenberg model and the reduced spin model (*6*). The reduced spin model based on the Ising model, which was developed by Emori *et al.* (*10*), seems to be suitable for the case of $Ba_2FeS_3$ and $Ba_2CoS_3$. According to this theory, the magnetic susceptibility is expressed as follows:

$$\chi_m = \frac{N\beta^2 g^2 S(S+1)}{3kT} \exp(J'/kT),$$

where

$$J' = \tfrac{4}{3} JS(S+1),$$

$\beta$ = Bohr magneton,
$k$ = Boltzmann constant,
$N$ = Avogadro number,
$J$ = intrachain interaction.

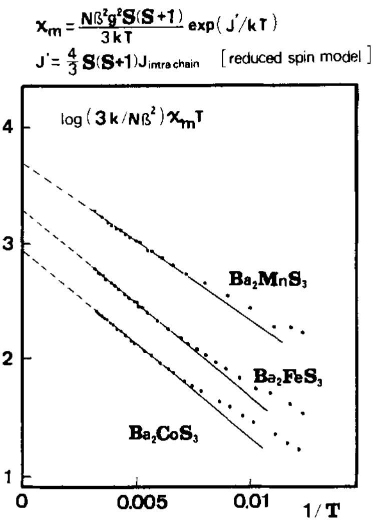

FIG. 2. Plot of $\chi$–$T$ relation using reduced spin model. The log $[3k\chi_m T/N\beta^2]$ vs $1/T$ curves show linear relation.

Plots of log $(3k\chi_m T/N\beta^2)$ vs $1/T$ for these three compounds are shown in Fig. 2. The slope of the linear portion $J'/k$ gives the value of the intrachain interaction. The intercept of the linear portion log $[g^2S(S+1)]$ gives the effective magnetic moment $p_{eff} = [g^2S(S+1)]^{1/2}$. Obtained values are listed in Table I. Intrachain interactions are antiferromagnetic with negative values of $J$. The values for $Ba_2MnS_3$ ($J/k = -12$ K) agree well with the results of Grey and Steinfink ($J/k = -11.5$ K, reduced spin model; $J/k = -12.3$ K, Heisenberg model). For $Ba_2FeS_3$ and $Ba_2CoS_3$, $|J/k|$ values (20 and 15 K, respectively) are larger than that of $Ba_2MnS_3$, corresponding to higher $T(\chi_{max})$, the temperature of maximum susceptibility. Effective magnetic moments, $P_{eff}$, are reasonable values for high-spin $Fe^{2+}$, $Co^{2+}$, and $Mn^{2+}$ ions. In Table I, the values of $T(\chi_{max})k/|J|$ and $\chi_{max}T(\chi_{max})/g^2$ are compared with the results of numerical calculations for one-dimensional antiferromagnetic model systems listed by de Jongh and Miedema (*8*).

### 2. $^{57}$*Fe Mössbauer Spectra*

$^{57}Fe$ Mössbauer spectra of $Ba_2FeS_3$ and $^{57}Fe$-doped $Ba_2CoS_3$ and $Ba_2MnS_3$ at 4.2 K, 77 K, and room temperature are shown in Figs. 3a, b, and c. Obtained parameters are listed in Table II.

At room temperature, the three spectra all show large quadrupole splittings, as is typical of high-spin $Fe^{2+}$ ions. Values of the isomer shift are comparable with those for tetrahedrally coordinated high-spin $Fe^{2+}$

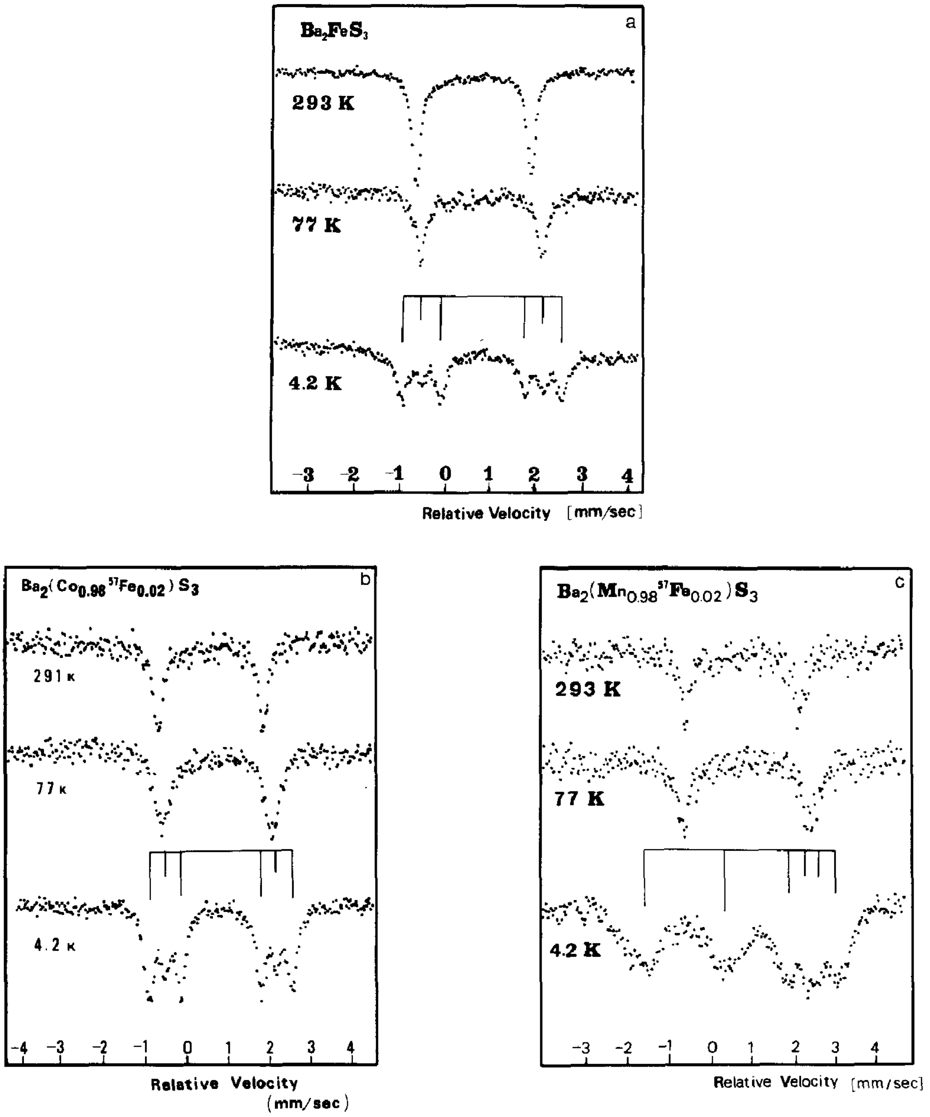

FIG. 3. $^{57}$Fe Mössbauer spectra of $Ba_2FeS_3$ (a) and 2 atom% $^{57}$Fe-doped $Ba_2CoS_3$ (b) and $Ba_2MnS_3$ (c). Calculated spectra fitted to those at 4.2 K are shown as stick diagrams.

ions in halides such as $(NMe)_2FeCl_4$ (*11*). This indicates the ionic character of $Fe^{2+}$ ions in these compounds. Absorption intensities of doublets are slightly asymmetrical. The anisotropic crystal structure (chain-like structure) suggests the possibility of Gordanski–Karyagin effect (*12*).

At 77 K, all spectra shown only doublets, which indicates that these compounds are paramagnetic at 77 K. This confirms that the rounded maxima at about 100 ~130 K in the $\chi$–$T$ curves do not correspond to any long-range magnetic ordering. The lineshapes of the absorptions at 77 K are rather broad compared with those at room temperature. For further discussion, however, we need Mössbauer spectra with better statistics.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA

| | $Ba_2FeS_3$ | $Ba_2CoS_3$ | $Ba_2MnS_3$ |
|---|---|---|---|
| 1. $M$–$M$ distance along chain (Å) | 4.25 | 4.20 | 4.30 |
| 2. $T(\chi_{max})$ (K) | 130 | 125 | 105 |
| 3. $\chi_{max}$ (emu/mole) | $7.73 \times 10^{-3}$ | $5.48 \times 10^{-3}$ | $1.45 \times 10^{-2}$ |
| 4. Intrachain interaction $J/k$ (K) | −20.5 | −15 | −12<br>(−11.5)[a] |
| 5. $p_{eff}$<br>[calculated][b] | 5.20<br>[4.90] | 4.35<br>[3.87] | 6.42<br>[5.92] |
| 6. $kT(\chi_{max})/\lvert J\rvert$ | | | |
| Observed | 6.3 | 8.3 | 8.75 |
| Heisenberg model | 7.1 | 4.75 | 10.6 |
| Ising model | 7.46 | 4.70 | 10.8 |
| 7. $\chi_{max}T(\chi_{max})/g^2$ | | | |
| Observed | 0.25 | 0.17 | 0.38 |
| Heisenberg model | 0.25 | 0.16 | 0.38 |
| Ising model | 0.28 | 0.18 | 0.41 |

[a] Value from Grey and Steinfink (*6*).

[b] Spin-only value.

TABLE II

MÖSSBAUER PARAMETERS

| | $Ba_2FeS_3$ | $Ba_2CoS_3$ | $Ba_2MnS_3$ |
|---|---|---|---|
| R.T. | | | |
| IS (mm/sec) | 0.65<br>(0.62)[a] | 0.60 | 0.63 |
| QS (mm/sec) | 2.58<br>(2.56) | 2.54 | 2.75 |
| 77 K | | | |
| IS (mm/sec) | 0.75<br>(0.75) | 0.72 | 0.83 |
| QS (mm/sec) | 2.71<br>(2.64) | 2.64 | 3.06 |
| 4.2 K | | | |
| IS (mm/sec) | 0.83 | 0.64 | — |
| QS (mm/sec) | 2.74 | 2.74 | 3.09 |
| $\theta$ (°) | 60 | 50 | 0 |
| $\eta$ | 0 | 0 | 0.4 |
| $H_{hf}$ (kOe) | 36 | 29 | 59 |

[a] Values in parentheses from Reiff *et al.* (*4*).

At 4.2 K all spectra show magnetic splitting, which is evidence for three-dimensional, long-range magnetic ordering due to interchain interactions. The change of magnetic behavior from one-dimensional to three-dimensional is typical of magnetic materials with low dimensionality, which is called "lattice dimensionality crossover" (*9*). Néel temperatures could not be determined by magnetic susceptibility measurements. Perhaps a thermal scan of Mössbauer spectra will be able to determine them. We intend to perform such a measurement.

The observed magnetic splitting at 4.2 K is characteristic of the coexistence of a magnetic hyperfine field $H_{hf}$ and an electric field gradient. The fit to calculated spectra and the evaluation of hyperfine parameters were performed using covenient Kündig's graphs (*13*). The obtained results are shown as stick diagrams in Figs. 3a, b, and c. The spectra of $Ba_2FeS_3$ and $^{57}$Fe-doped $Ba_2CoS_3$ are very similar. The spectra are reproduced assuming that the asymmetry factor $\eta = 0$, the angle between the EFG principal axis and $H_{hf}$ $\theta = 60°$, QS = 2.74 mm/sec, $H_{hf} = 36$ kOe for $Ba_2FeS_3$, and $\eta = 0$, $\theta = 50°$, QS = 2.74 mm/sec, $H_{hf} = 29$ kOe for $^{57}$Fe-doped $Ba_2CoS_3$. The observed line intensities approximately agree with those of calculated spectra. The value of $H_{hf}$ for $^{57}$Fe-doped $Ba_2CoS_3$ is smaller than that for $Ba_2FeS_3$, reflecting the smaller magnetic moment. The spectrum of $^{57}$Fe-doped $Ba_2MnS_3$ shows different splitting from those of the other two compounds. The observed spectrum is reproduced assuming that $\eta = 0.4$, $\theta = 0°$, QS = 3.09 mm/sec, and $H_{hf} = 59$ kOe, but line intensities do not agree so well with those of calculated spectra. Furthermore, the lineshape is rather broad, indicating that the distribution of $H_{hf}$ is probably due to inhomogeneity of the sample.

## Conclusion

Results of magnetic susceptibility and $^{57}$Fe Mössbauer spectra measurements for the linear chain compounds $Ba_2MS_3$ ($M$ = Fe, Co, Mn) showed that these compounds are quasi-one-dimensional antiferromagnets. Thus, the quasi-one-dimensional magnetic behavior similar to that of $ABX_3$-type halides (*8*) has been confirmed in these sulfides where the transition metal cautions are tetrahedrally coordinated. At lower temperatures these compounds order antiferromagnetically due to interchain interactions. $^{57}$Fe Mössbauer spectra at 4.2 K were interpreted as due to the coexistence of a small magnetic hyperfine field and a large quadrupole interaction.

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