

## Magnetic and Mössbauer studies of phase transitions and mixed valences in bornite ( $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$ )

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In this paper, measurements of the temperature-dependent magnetic susceptibility ( $\chi$ ) and Mössbauer spectrum (MS) are reported in natural samples of bornite,  $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$ . The magnetic studies on two samples, between 4.2 and 300 K, show a magnetic phase transition to an antiferromagnetic state with the Néel temperature  $T_N = 67.5$  K. However, the behavior of  $\chi$  vs  $T$  is not that of a simple antiferromagnet. The Mössbauer data, taken between 12.8 and 300 K, show the presence of high-spin  $\text{Fe}^{3+}$  and low-spin  $\text{Fe}^{2+}$ , whose concentrations change as a function of temperature ( $\text{Fe}^{2+}$  increases with increasing temperatures). Based on this and the temperature-dependent  $\text{Fe}^{3+}$  MS linewidth, it is proposed that bornite consists of fluctuating valences between  $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$  and  $\text{Cu}^{1+} \rightleftharpoons \text{Cu}^{2+}$ , the rate of electron hopping between these states being strongly temperature dependent. The observed temperature dependence of  $\chi$  is in qualitative agreement with this model.

### I. INTRODUCTION

Bornite ( $\text{Cu}_5\text{FeS}_4$ ) is a copper ore mineral of considerable economic importance. Depending on temperature, three polymorphs of bornite are known to exist.<sup>1,2</sup> Above 500 K, bornite is cubic (space group  $Fm\bar{3}m$ ,  $a = 5.50$  Å) with antiferrofluorite structure. On cooling below 500 K, this form changes to a metastable cubic form with double the unit cell ( $a = 10.94$  Å). Finally, on cooling below 450 K, the low-temperature stable form is obtained with cell dimensions  $a = 10.95$ ,  $b = 21.86$ , and  $c = 10.95$  Å with space group  $Pbca$  and 16  $\text{Cu}_5\text{FeS}_4$  molecules per unit cell.<sup>2</sup> Only the low-temperature phase occurs naturally.

Studies of the electrical and magnetic properties of natural and synthetic bornite have been reported by several groups.<sup>3-5</sup> The magnetic susceptibility  $\chi$  of bornite above 77 K has been found to obey the Curie-Weiss law, viz.  $\chi = N\mu^2/3k_B(T + \Theta)$ , where  $N$  is the number of magnetic ions/mole with moment  $\mu$ ,  $k_B$  is the Boltzmann constant, and  $\Theta$  is the Curie-Weiss temperature. For the low-temperature phase (which is the one that is studied in this paper), Allais *et al.*<sup>3</sup> deduced values of  $\Theta = 440$  K and  $\mu = 6.4\mu_B$  ( $\mu_B$  is the Bohr magneton). Takeno *et al.*<sup>4</sup> and Townsend *et al.*<sup>5</sup> have, respectively, reported  $\Theta = 664$  and 450 K, and  $\mu = 6.68\mu_B$  and  $6.3\mu_B$ . These values are for stoichiometric  $\text{Cu}_5\text{FeS}_4$ . For  $\text{Cu}_{4.9}\text{Fe}_{1.1}\text{S}_4$  and  $\text{Cu}_{5.1}\text{Fe}_{0.9}\text{S}_4$ , respectively, Takeno *et al.*<sup>4</sup> reported  $\Theta = 82$  and 440 K, and  $\mu = 4.51\mu_B$  and  $5.38\mu_B$ . Thus, nonstoichiometry tends to reduce both  $\mu$  and  $\Theta$ , the effect being more pronounced when Fe is in

excess and Cu is deficient. Except for Townsend *et al.*,<sup>5</sup> who measured  $\chi$  between 4.2 and 300 K, the other two groups measured  $\chi$  only above 77 K.

From the Mössbauer studies down to 4.2 K, Allais and Curien<sup>3</sup> observed the magnetic ordering temperature in bornite to be 65 K, although no details are given in their paper about the Mössbauer work which led them to this ordering temperature. Recently Townsend *et al.*<sup>5</sup> reported a peak in the curve of  $\chi$  vs  $T$  at a temperature of  $76 \pm 2$  K for bornite. They associated this peak with the ordering temperature. They also reported Mössbauer measurements for natural and synthetic bornite for several temperatures below 65 K. At 65 K, the hyperfine splitting characteristic of magnetic ordering is not observed, whereas their Mössbauer spectra at 62 K and lower temperatures definitely show evidence of magnetic ordering. Townsend *et al.*<sup>5</sup> also reported the presence of a paramagnetic ion in the ordered state which they attributed to the occurrence of partial disorder or vacancy clustering.

In the work reported in this paper, we have carried out temperature-dependent magnetic susceptibility and Mössbauer measurements in natural samples of bornite. Magnetic measurements were made on two natural samples, between the temperatures of 4.2 and 300 K. Special emphasis is given to accurately determine the Néel temperature  $T_N$  by taking data at close temperature intervals and under several different conditions of cooling the sample. In the work of Townsend *et al.*,<sup>5</sup> the  $\chi$  data were taken only at wide temperature intervals (10 to 15 K) near  $T_N$ . Also, their method of judging  $T_N$  from the peak in  $\chi$  vs  $T$

curve would yield higher value of  $T_N$ , since it is now known that  $T_N$  is determined by the inflexion point in the  $\chi T$  vs  $T$  curve. Our careful measurements and analysis have yielded  $T_N = 67.5 \pm 0.5$  K for bornite. We also discuss the nature of the temperature dependence of  $\chi$  and the diamagnetic contribution to  $\chi$  (ignored by others) is considered. A careful analysis of the temperature dependence of the Mössbauer spectrum taken between 12.8 and 300 K is also presented. This analysis has led us to conclude that the spectrum is due to valence fluctuations between  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ . The observed temperature dependence of  $\chi$  is consistent with this interpretation. This conclusion is quite different from the model of vacancy clustering advanced by Townsend *et al.*<sup>5</sup> In Secs. II–IV, details of these studies are presented.

## II. EXPERIMENTAL DETAILS

The magnetic susceptibility measurements were carried out on two natural samples: sample A of unknown origin provided by Dr. Khan and Dr. McCormick of the Department of Chemistry, West Virginia University, and sample B, provided by Dr. Pierce of Arizona State University, on a piece of which a high-resolution electron microscopy study has been carried out.<sup>6</sup> Most of the detailed studies were carried out on sample A, since sample B appears to contain an impurity, most likely  $\alpha\text{-Fe}_2\text{O}_3$ . The magnetic-susceptibility measurements were carried out with a Faraday balance, details of which have been described in a recent paper.<sup>7</sup> The absolute precision in  $\chi$  is about 1.5% and the relative precision about 0.3%. The powdered samples were wrapped in aluminum foil and the data presented in this paper have been corrected for the Al-foil background according to the method described elsewhere.<sup>7</sup> A chemical analysis of the sample A (done by Galbraith Laboratories, Knoxville, Tenn.) yielded the composition  $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$ .

The Mössbauer spectrometer used in this work was a conventional constant acceleration spectrometer. The source was a 50-mC  $^{57}\text{Co}:\text{Pd}$ . The temperature-dependent measurements were carried out by means of a closed cycle helium refrigerator with a temperature stability of better than 0.1 K. The Mössbauer spectra were analyzed using a nonlinear least-squares fit program and assuming Lorentzian line shapes. All the isomer-shift (IS) values are given with reference to that of  $\alpha$ -iron at room temperature.

## III. EXPERIMENTAL RESULTS

### A. Magnetic studies

The magnetic field ( $H$ ) dependence of the magnetization ( $M$ ) of sample A was checked at several tem-

peratures between 295 and 4.2 K. Above about 150 K,  $M$  varied linearly with  $\bar{H}$  (up to the available field of 10 kOe), whereas below this temperature,  $M$  varied nonlinearly with  $\bar{H}$ . In Fig. 1, we have plotted  $M$  vs  $\bar{H}$  at 4.2 K and in the inset the observed hysteresis is also shown. These results suggest that the measured  $\chi$  depends on  $\bar{H}$ , and on the previous magnetic history of the sample.

In carrying out the  $\chi$  measurements, the sample was usually cooled to 77 or 4.2 K and the temperature-dependent data were then taken by increasing the temperatures. In Fig. 2,  $\chi$  vs  $T$  data are plotted for two different experimental conditions. In one case, the sample was cooled from 300 to 4.2 K in the residual field ( $\sim 70$  Oe) of the electromagnet. Without increasing  $\bar{H}$  beyond 200 Oe at any time,  $\chi$  vs  $T$  data at 200 Oe were taken from 4.2 to 300 K. In the second case, the sample was cooled to 4.2 K as before, followed by the field-dependence measurements of Fig. 1. The field was then lowered to 200 Oe and the  $\chi$  vs  $T$  data taken (at 200 Oe) from 4.2 to 300 K. Below about 65 K, the two procedures yield different results (Fig. 2), whereas above this temperature, the two measurements essentially coincide. The susceptibility peaks near 72 K, although the peak magnitudes for the two cases are slightly different.

In the results of Fig. 2, there are several regions of interest. From 300 to about 140 K,  $\chi$  varies smoothly, whereas below 140 K, there is a rather dramatic increase in  $\chi$ , its value increasing by nearly a factor of 3 between 140 and 72 K. Below 65 K,  $\chi$  values are different for the two cases discussed above. In a later section we examine each of these regions separately.

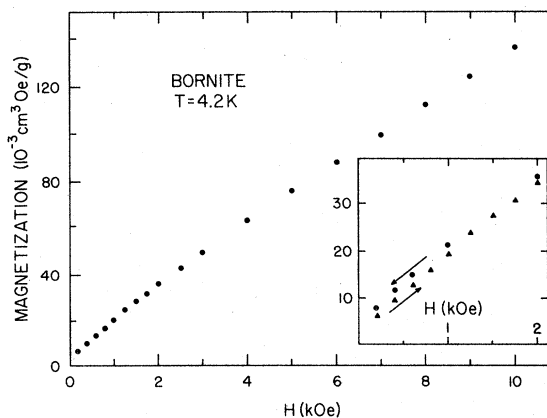


FIG. 1. Magnetization variation with magnetic field in bornite, after cooling the sample to 4.2 K in a low field ( $\sim 70$  Oe). The inset shows the observed hysteresis.

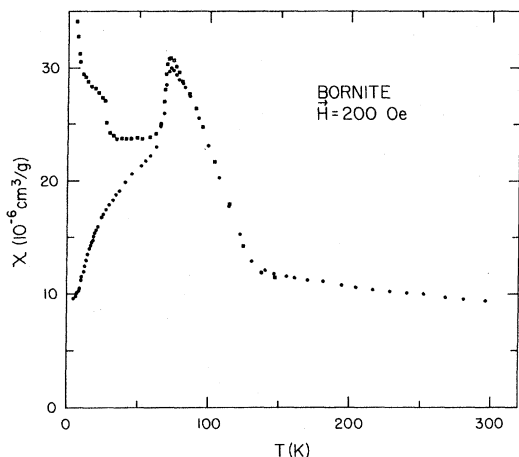


FIG. 2. Temperature dependence of magnetic susceptibility of bornite subjected to two different conditions. The lower curve (circles) is obtained when the sample is cooled in a very low field ( $\sim 70$  Oe) and the data taken with 200-Oe field. The upper curve (squares) is obtained on cooling the sample in  $\sim 70$ -Oe field, subjected to fields up to 10 kOe at 4.2 K and then  $\chi$ - $T$  data are taken at 200 Oe.

### B. Mössbauer studies

At room temperature, the Mössbauer spectrum of bornite (sample A) shows a slightly asymmetric single line with  $\Delta_{\text{IS}} = 0.41 \pm 0.02$  mm/s. As the temperature is lowered, we observed an increase in the asymmetry of the line, especially below 140 K. Below 68 K, we observed the onset of magnetic order. In Fig. 3, the Mössbauer spectra of bornite, between the temperatures of 69.8 and 12.8 K, are shown. The magnetic hyperfine splitting at low temperatures is  $342 \pm 2$  kOe and the  $\Delta_{\text{IS}} = 0.55 \pm 0.03$  mm/s. This spectrum is identified as that of  $\text{Fe}^{3+}$ , but with a large reduction in the hyperfine field from that of the ionic  $\text{Fe}^{3+}$  (550 kOe). This reduction is attributed to the covalency effects. Besides the  $\text{Fe}^{3+}$  spectrum we observed a doublet with an  $\Delta_{\text{IS}} = 0.40 \pm 0.03$  mm/s and with a quadrupole splitting  $\Delta_{\text{QS}} = 0.64 \pm 0.03$  mm/s. We attribute this doublet to the low-spin  $\text{Fe}^{2+}$  in a noncubic environment. The QS is temperature independent between 57.7 and 12.8 K and no magnetic moment is present at the iron ion in this doublet.

## IV. ANALYSIS AND DISCUSSION

### A. Determination of $T_N$

Townsend *et al.*<sup>5</sup> associated the peak in the susceptibility as the onset of magnetic order. Fisher<sup>8</sup> has shown that the peak in  $\chi$  occurs at a temperature 5 to

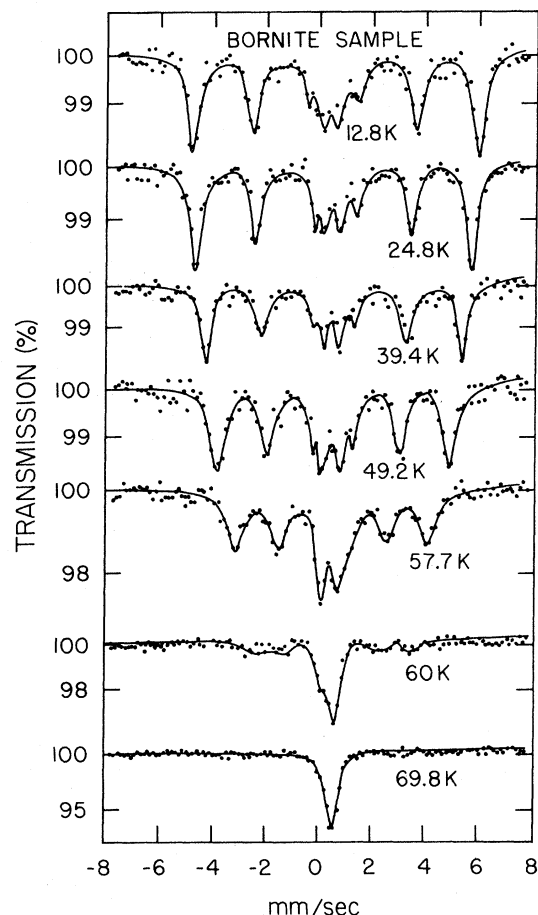


FIG. 3. Mössbauer spectra of bornite at various temperatures. The continuous line is the least-square fit to the data.

10% higher than the position of  $T_N$ , the latter being correctly determined by the position of the maximum in  $\partial(\chi T)/\partial T$ . In Fig. 4, we have plotted  $\chi T$  vs  $T$  and the computed  $\partial(\chi T)/\partial T$ .  $\partial(\chi T)/\partial T$  was obtained by computer fitting the data ( $\chi T$ ) to a second-order polynomial choosing four consecutive data points at a time, evaluating the slope at the median temperature, and then sliding the curve by one point for the next operation. The position of the sharp peak occurs at  $67.5 \pm 0.5$  K, which we associate with  $T_N$  for bornite. Irrespective of the way in which the sample was cooled, the peak always occurred at 67.5 K. This value of  $T_N$  is not inconsistent with the data of Townsend *et al.*,<sup>5</sup> since their method of determining  $T_N$  was only approximate as noted above, and secondly, their data points (as presented in their paper) were taken at about 10-K intervals so that an accurate value of  $T_N$  is simply not possible in such a case.

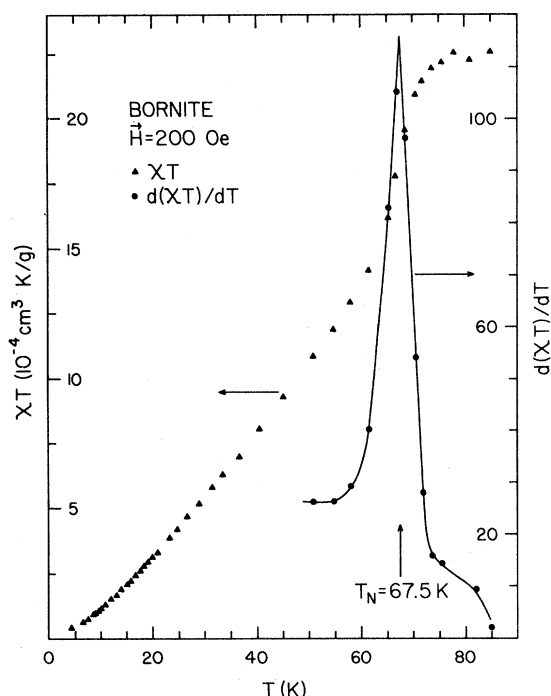


FIG. 4. Diagram showing the method adopted in determining  $T_N$  of bornite.

### B. Paramagnetic susceptibility

In Fig. 5, the inverse molar susceptibility of bornite is plotted against temperature. In general,  $\chi$  must be corrected for the diamagnetic contribution. For bornite we have used  $|\chi_d| = 0.4 \times 10^{-6} \text{ cm}^3/\text{g}$ ,<sup>9</sup> so that  $\chi$  of Fig. 5 equals the measured  $\chi$  plus  $|\chi_d|$ . Other investigators<sup>3-5</sup> have ignored  $\chi_d$ , whose estimated magnitude is about 4% of the measured  $\chi$  near 300 K. Above about 150 K,  $\chi^{-1}$  vs  $T$  is linear, yielding the Curie-Weiss constant  $\Theta = 456 \text{ K}$  and  $\mu = 5.4\mu_B$ . These values are similar to those determined by others, except our value of  $\mu$  is a little smaller.

We have attempted to fit the paramagnetic susceptibility to an expression expected for a ferrimagnet,<sup>10</sup> given by

$$\frac{1}{\chi} = \frac{T}{C} + \frac{1}{\chi_0} - \frac{\sigma}{T - \Theta_a}, \quad (1)$$

where  $C$ ,  $\chi_0$ ,  $\sigma$ , and  $\Theta_a$  are constants determined by the distribution and interaction of the magnetic ions in the system. The major difference between Eq. (1) and the Curie-Weiss law is the third term on the right-hand side which increases  $\chi$  when  $T$  approaches  $\Theta_a$ . Assuming that  $\sigma/(T - \Theta_a)$  term is insignificant above about 160 K, then one obtains  $\chi_0^{-1} \approx 124 \text{ cm}^{-3}/\text{mole}$  and  $C = 3.681 \text{ cm}^3\text{K}/\text{mole}$ . From the measured  $\chi$  and the above values of  $\chi_0^{-1}$  and  $C$ ,

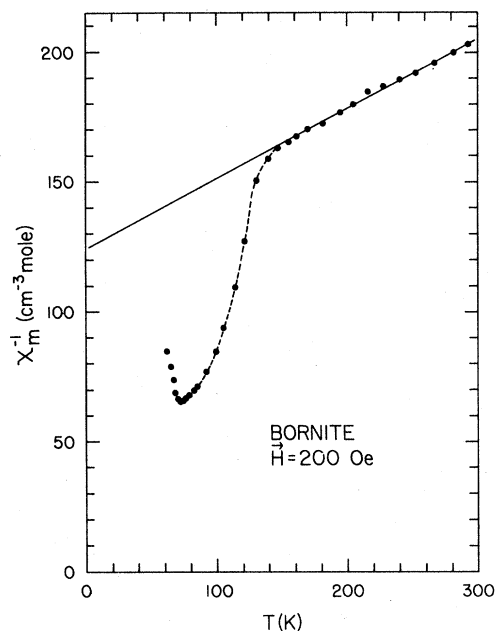


FIG. 5. Reciprocal molar susceptibility (corrected for diamagnetism) plotted vs temperature to evaluate  $\Theta$  and  $\mu$ .

$\sigma/(T - \Theta_a)$  term was estimated from Fig. 5 for  $T < 155 \text{ K}$ . If the inverse of this term is plotted against  $T$ , one should get a straight line according to Eq. (1), if  $\sigma$  and  $\Theta_a$  are independent of temperature. The results varied enormously from a straight-line behavior, suggesting that bornite is not an example of a simple ferrimagnet. The magnetization behavior below  $T_N$  is also not that of a typical ferrimagnet. Later we argue that bornite is an antiferromagnet, but one with its moment changing with temperature.

### C. Magnetic susceptibility below $T_N$

The variation of  $\chi$  with temperature below  $T_N$  is shown in Fig. 2. The higher susceptibility observed for the case after the sample is magnetized at the higher field of about 10 kOe is simply due to the remanent magnetization (see inset of Fig. 1). Somewhat similar behavior is observed (not shown in Fig. 2) if the sample is cooled from above  $T_N$  in several kOe and the susceptibility measured at  $H = 200 \text{ Oe}$ . The susceptibility of the virgin state decreases as  $T$  decreases below  $T_N$ , qualitatively similar to the expectation for a simple antiferromagnet. However, the detailed nature of the curve is quite different, with a hump near 35 K and an inflexion point near 10 K. (The latter becomes quite evident if one computes  $\partial\chi/\partial T$ .) This is essentially the same temperature where Townsend *et al.*<sup>5</sup> had also seen an inflexion in the  $\chi$  vs  $T$  curve. They had suggested that this may

be due to a rearrangement of the magnetic order, although no experimental evidence for this was available. We note that in the magnetized sample also (upper curve of Fig. 2) there are significant changes in the  $\chi$  vs  $T$  curve near 35 and 10 K, the temperatures of interest noted above.

#### D. Temperature dependence of the Mössbauer spectra

First we note that there are several areas of agreement between our observations and those of Townsend *et al.*<sup>5</sup> The magnetic hyperfine field of 342 kOe and the  $\Delta_{IS} = 0.55 \pm 0.03$  mm/sec at low temperatures for  $\text{Fe}^{3+}$  are in excellent agreement with those reported in Ref. 5. The major area of disagreement between the two studies is the interpretation of the additional Mössbauer lines observed in both studies. Townsend *et al.*<sup>5</sup> identify only a single line (in addition to the  $\text{Fe}^{3+}$  spectrum) which they attribute to metal deficient domains in the crystal. With the higher velocity resolution of our experiment, we identified a doublet with a  $\Delta_{QS} = 0.64 \pm 0.03$  mm/sec. The metal cations are in tetrahedral environment, the presence of a quadrupole splitting is evidence of Jahn-Teller distortion. We consider this doublet to be low-spin  $\text{Fe}^{2+}$  since no magnetic moment is present at the cation site. This is a situation somewhat similar to  $\text{Fe}^{2+}$  in  $\text{FeS}_2$ ,<sup>11</sup> where the absence of a magnetic moment was shown by applying an external magnetic field. Analysis of the temperature dependence of the Mössbauer spectra described below suggests valence fluctuations between  $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ .

It is well known that the Mössbauer effect is a powerful tool to study dynamic phenomena<sup>12,13</sup> if the rate of change for iron is of the order of  $10^9$  to  $10^7$   $\text{sec}^{-1}$ . To take advantage of this, we have measured the spectral areas for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  below  $T_N$ , based on the interpretation described in the above paragraph and the results are shown in Fig. 6. The Debye-Waller factors for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  are considered equal for this analysis. However, any difference in Debye-Waller factor will have only a slight influence on the overall behavior of the ratio  $A(\text{Fe}^{2+})/A(\text{Fe}^{3+})$ . From Fig. 6 it is clear that the concentration of  $\text{Fe}^{3+}$  increases at the expense of  $\text{Fe}^{2+}$  as the temperature is lowered. We interpret this as due to the hindrance of the electron hopping at the lower temperatures since not enough thermal energy is available to form the excited state (*viz.*,  $\text{Fe}^{2+}$ ). Thus our model suggests bornite to be a mixed valence system, with electron hopping taking place both between  $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$  and  $\text{Cu}^{1+} \rightleftharpoons \text{Cu}^{2+}$ , the latter being required by charge neutrality.

As further evidence of the dynamics of

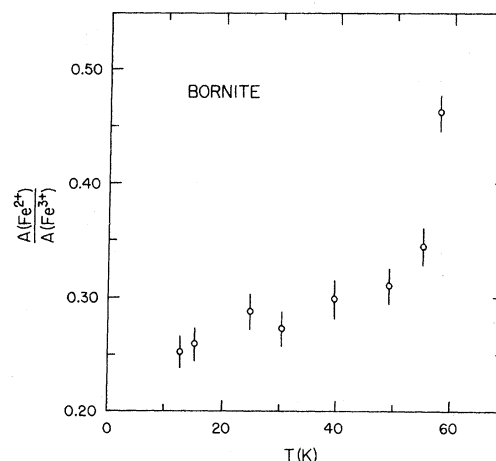


FIG. 6. Ratio of the Mössbauer spectral areas for  $\text{Fe}^{2+}/\text{Fe}^{3+}$  vs temperature.

$\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ , we have observed broadening of the Mössbauer  $\text{Fe}^{3+}$  hyperfine lines above about 35 K and the results are shown in Fig. 7. This broadening, also indicated in the work by Townsend *et al.*,<sup>5</sup> was attributed by them to small changes in temperature during the measurements. On the contrary, we attribute this broadening to dynamics of electron hopping rate of which is expected to increase as temperature increases, thereby broadening the lines. It is noted that the onset of line broadening coincides with the increase in the spectral area of  $\text{Fe}^{2+}$ . In Fig. 8 we have plotted  $H(T)/H(0)$  vs  $T/T_N$  (using  $T_N = 67.5$  K as determined from  $\chi$  data discussed earlier) where  $H(0) = 342$  kOe is the hyperfine field in the limit of  $T = 0$  K.

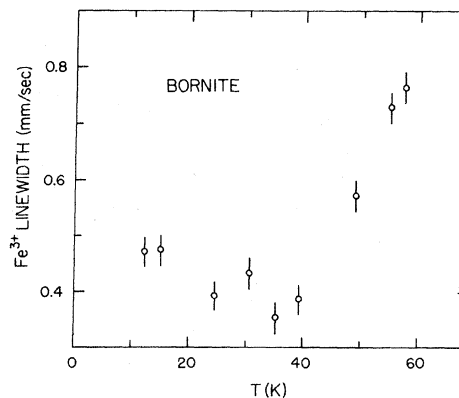


FIG. 7. Linewidth of the external lines of  $\text{Fe}^{3+}$  in bornite vs temperature.

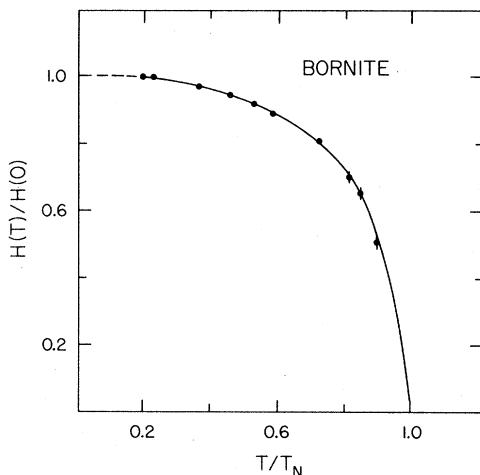


FIG. 8. Ratio of the reduced magnetic hyperfine field  $H(T)/H(0)$  vs reduced temperature  $(T/T_N)$ .

#### E. Nonstoichiometry, magnetic susceptibility, and valence fluctuations

As noted in Sec. II, the sample used in our work has the composition  $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$ , whereas Townsend *et al.*<sup>5</sup> indicate the composition of their sample to be nearly stoichiometric ( $\text{Cu}_{5.01}\text{Fe}_{0.98}\text{S}_4$ ). We have already noted why the  $T_N$  determined in this work is consistent with the results of Townsend *et al.*<sup>5</sup> However, the absolute values of  $\chi$  for the two cases are somewhat different; the  $\chi$  values reported in Ref. 5 at room temperature are about 35% higher than the ones shown in Fig. 2, whereas the peak value near  $T_N$  is considerably higher in our case. One reason for this difference may be that we have measured the initial  $\chi$  (at 200 Oe) which for  $T_N < T < 140$  K is larger than the  $\chi$  measured at the higher fields. Below  $T_N$ , the initial  $\chi$  is lower if the sample is cooled in nearly zero field (Fig. 2). Unfortunately Townsend *et al.*<sup>5</sup> do not indicate under what experimental conditions their measurements were carried out.

Next we consider the effects of fluctuating valences on  $\chi$ . As noted earlier, below about 140 K,  $\chi$  becomes field dependent and increases with lowering temperatures quite sharply. This is essentially the same region in which the Mössbauer line becomes increasingly asymmetric. Following the model of fluctuating valences proposed earlier, we suggest that the dramatic rise in  $\chi$  below 140 K is due to an increase in the concentration of  $\text{Fe}^{3+}$  ions. Below  $T_N$ , the situation is more complicated due to at least two processes simultaneously in action: the normal decrease of  $\chi$  for an antiferromagnet with decreasing temperatures and the changing concentration of  $\text{Fe}^{3+}$

Note that the anomalies in  $\chi$  (Fig. 2) and the Mössbauer spectrum (Figs. 6 and 7) occur essentially in the same temperature region below  $T_N$ . However, it is not possible to provide a quantitative explanation for the temperature dependence of  $\chi$  below 140 K at present.

We also measured  $\chi$  for sample B (see Sec. II). This sample was cooled to about 16 K in  $\bar{H} = 1$  kOe, followed by  $\chi$  vs  $T$  measurements (Fig. 9) at 1 kOe. The results show a peak in  $\chi$  near 70 K, essentially the same temperature as in Fig. 2. Thus, we conclude that  $T_N$  for the two samples is nearly the same. In Fig. 9, there is a second inflexion point near 260 K. Since  $\alpha\text{-Fe}_2\text{O}_3$  undergoes weak ferromagnetic-antiferromagnetic transition on cooling through 260 K,<sup>14</sup> it is very likely that  $\alpha\text{-Fe}_2\text{O}_3$ , as an impurity in this sample, is the source of the anomaly near 260 K. The main purpose of presenting Fig. 9 is to demonstrate that samples from two different sources have yielded the same  $T_N$ .

The molecular weights of  $\text{Cu}_{4.5}\text{Fe}_{1.2}\text{S}_{4.7}$  and  $\text{Cu}_5\text{FeS}_4$  do not differ by more than 0.4% so that the value of  $\mu = 5.4\mu_B$  already evaluated (Fig. 5) is not affected. This value is lower than that expected for  $\text{Fe}^{3+}$  ( $= 5.9\mu_B$ ), whereas those reported by others for stoichiometric compounds<sup>3-5</sup> ( $\sim 6.4\mu_B$ ) are higher. However, they did not include the diamagnetic contribution in their analysis which would affect by several percent the value of  $\mu$ . However the rest of the discrepancy is probably due to nonstoichiometry. If we assume that bornite contains a mixture of  $\text{Fe}^{3+}$  ( $\mu = 5.9\mu_B$ ) and low-spin  $\text{Fe}^{2+}$  ( $\mu = 0$ ) and conse-

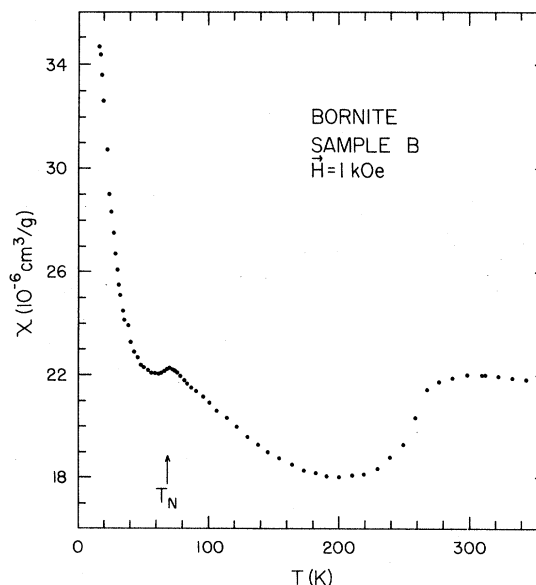


FIG. 9. Temperature variation of magnetic susceptibility of bornite (sample B).

quently, a mixture of  $\text{Cu}^{1+}$  ( $\mu = 0$ ) and  $\text{Cu}^{2+}$  ( $\mu = 1.73\mu_B$ ), then the lower values of  $\mu$  observed in this work and by Takeno *et al.*<sup>4</sup> for nonstoichiometric bornite can be understood.

#### V. CONCLUDING REMARKS

The results presented in this paper show that bornite orders antiferromagnetically with  $T_N = 67.5$  K and that the valence of the constituent metal ions are fluctuating between  $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$  and  $\text{Cu}^{1+} \rightleftharpoons \text{Cu}^{2+}$ , the rate of electron hopping between different charge states being strongly temperature dependent. This results in a change in the concentration of  $\text{Fe}^{3+}/\text{Fe}^{2+}$  and  $\text{Cu}^{1+}/\text{Cu}^{2+}$  as the temperature changes. However, there are several observations which require further studies for clarification. For example, the exact nature of the antiferromagnetic ordering is still not known. Associated with this is the unresolved question of a second phase transition near 10 K and the

observed hysteresis below  $T_N$ . Are these effects due to a metamagnetic transition? The problem of the rather large magnetic moment ( $= 6.4\mu_B$ ) observed by others above  $T_N$  in stoichiometric bornite needs to be understood better. In our view these questions can be resolved satisfactorily only if careful studies on stoichiometric single crystals become available.

#### ACKNOWLEDGMENTS

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