OBSERVATION OF THE ANTIFERROMAGNETIC TRANSITION IN THE LINEAR CHAIN COMPOUND KFeS₂ BY MAGNETIC SUSCEPTIBILITY AND HEAT CAPACITY MEASUREMENTS

D.C. Johnston, S.C. Mraw and A.J. Jacobson

Corporate Research-Science Laboratories, Exxon Research and Engineering Company, P.O. Box 45, Linden, NJ 07036, U.S.A.

(Received 3 November 1981 by H. Suhl)

Magnetic susceptibility (χ) measurements and the first heat capacity measurements on KFeS₂ are reported. The data were obtained on a specially purified sample over the temperature ranges 10–360 K and 225–296 K, respectively. Both measurements revealed small but distinct singularities at the Néel temperature $T_N \approx 253$ K; extensive short range ordering above T_N was also evident from these data. The present work shows that the intrinsic $\chi(T)$ of KFeS₂ was largely masked by that from magnetic impurities in previous χ studies of this compound.

1. INTRODUCTION

THE COMPOUND KFeS₂ contains chains of edgeshared FeS₄ tetrahedra which are separated from and bound to each other with K atoms [1, 2]. Because both the first and second neighbor intrachain separations of the Fe atoms (2.70 and 5.40 Å) are much shorter than the smallest interchain separation (6.5 Å), the magnetic properties would be expected to be dominated by the intrachain spin interactions. This was confirmed through magnetic susceptibility measurements which showed that the susceptibility increases monotonically with temperature from 300 to 675 K, reflecting shortrange antiferromagnetic order along the chains [3]. However, long-range colinear antiferromagnetic order does develop at $T_N \approx 250 \,\mathrm{K}$ as shown from recent neutron diffraction measurements [2, 4]; the interchain magnetic interactions are therefore also significant.

Extensive ⁵⁷Fe Mössbauer, [5–16] electron paramagnetic resonance (EPR) [17-20], magnetic susceptibility [2, 3, 7, 10, 14, 17, 21] and optical absorption spectroscopy [22] measurements have been reported for KFeS₂ and related AFeS₂ compounds with A =Li, Na, Rb and Cs. The results of EPR and susceptibility measurements on KFeS₂ by different investigators are conflicting. The susceptibility was reported to be temperature independent [3] or to increase with decreasing temperature [2, 7] below T_N , in contrast to the behavior expected for an antiferromagnet. In addition, each of the susceptibility measurements on KFeS₂ [2, 3, 7, 10, 17] failed to reveal any anomaly at T_N . These results suggest that magnetic impurities may have strongly influenced the data obtained from the EPR and susceptibility measurements.

We report herein a new technique for preparation

of polycrystalline KFeS₂ which substantially reduces the levels of paramagnetic and ferromagnetic impurities below those which we have found to arise from the preparation method usually used by other workers. High precision magnetic susceptibility and heat capacity studies of KFeS₂ synthesized using the new technique were carried out to clarify the intrinsic thermodynamic properties of this material and, in particular, to examine the thermal and magnetic manifestations of the antiferromagnetic ordering transition at T_N . The results of these studies are summarized here.

2. SAMPLE PREPARATION

Two samples of $KFeS_2$ were prepared. The first was made using the method [23] employed by most previous workers to synthesize $A \operatorname{FeS}_2$ compounds. 2 g iron powder (JMC Puratronic, 1 ppm Co detected), 10g K₂CO₃ (MCB, 5 ppm Fe detected) and 11 g sulfur (A.D. MacKay, 99.999%) were fused in an alumina crucible at 900°C for 4 hr under a nitrogen atmosphere. The product was cooled to room temperature over a period of 16 hr, then extracted with water. This procedure gave small permanganate-colored, needle-shaped crystals which were further washed with water and acetone and air dried. Magnetization vs. applied magnetic field isotherms obtained for this sample at 298 and 77 K were nonlinear at low fields, but linear in fields of 5-8 kG. The zero-field magnetization intercepts obtained by extrapolating the high field linear data to zero field were 0.36 and 2.96 G-cm³ mole⁻¹, respectively; the latter is equivalent to the saturation moment of 240 molar ppm of ferromagnetic iron metal impurities. The differential high field susceptibilities (χ) were 5.5×10^{-4} and 8.2×10^{-4} cm³ mole⁻¹, respectively,

similar to previous results [3]. In view of the χ data to be presented below for the second KFeS₂ sample and assuming that the paramagnetic impurities giving rise to the temperature dependence of χ in the first sample have a Curie-Weiss susceptibility, the computed level of paramagnetic impurities in the first sample is equivalent to 2.3 mol % high spin Fe³⁺ impurities. These ferromagnetic and paramagnetic impurity levels are many orders of magnitude larger than known to be present in the starting materials; hence a second phase or phases had to be present containing Fe. We suspected that leaching the KFeS₂ crystals from the solidified flux with water resulted in the formation of a thin surface layer of paramagnetic and ferromagnetic oxides and/or hydroxides. Since it is known that KFeO₂ converts to KFeS₂ under H₂S at elevated temperatures [24], the second sample of $KFeS_2$ was synthesized from the first by heating in a stream of H_2S at 500°C for 4 hr, to convert the surface impurity film back into KFeS₂. The resulting product was found to be virtually free of magnetic impurity phases, as described below. The detailed magnetic susceptibility and heat capacity data presented below were obtained on this second KFeS₂ sample. The sample was not exposed to air at any time following the H₂S treatment.

3. RESULTS AND DISCUSSION

Magnetization data were obtained using the Faraday method between 10 and 360 K, and with applied fields of 0-8 kG. The accuracies of the measured susceptibility and temperature were 1-2% and 1 K, respectively. Magnetization vs. applied magnetic field isotherms at 298 and 77 K revealed magnetic impurity saturation magnetizations which were the same within experimental error $[(5.3 \pm 0.3) \times 10^{-2} \text{ G-cm}^3 \text{ mole}^{-1}]$, equivalent to that of 4.3 molar ppm of ferromagnetic iron metal impurities. High precision susceptibility data were obtained by measuring the magnetization in a fixed applied field of 6.35 kG upon sweeping the temperature at less than 1 K min⁻¹, and correcting the measured values for the ferromagnetic impurity contribution; this correction amounted to 2.9-4.2%, depending on the temperature.

The magnetic susceptibility of $KFeS_2$ is plotted vs. temperature in Fig. 1 for the temperature range 10-360 K. Several features of these data are noteworthy.

(1) The susceptibility increases monotonically with temperature from 40 to 360 K, in contrast to that of sample 1 above and to literature data [2, 3, 7].

(2) A small upturn occurs in the data below 40 K, probably due to remnants of paramagnetic impurities; this impurity level is equivalent to about 20 molar

ppm of high spin Fe³⁺ impurities.

(3) Most importantly, the occurrence of the antiferromagnetic transition is clearly seen at $252 \pm 2 \text{ K}$ via a slope discontinuity at that temperature; the slope changes from 5.5×10^{-7} to $4.1 \times 10^{-7} \text{ cm}^3 \text{ (mole-K)}^{-1}$ upon traversing T_N from below.

(4) Above T_N , χ continues to increase with temperature, reflecting short-range antiferromagnetic order along the iron chains; to within the experimental precision, χ varies linearly with temperature between 252 and 300 K. After correcting for the paramagnetic impurity contribution, the data below T_N can be fitted reasonably well with a simple power law of the form $\chi = A + BT^n$, with $n = 1.8 \pm 0.1$; the exponent is close to the value of 2 predicted by lowest order spin wave theory [25].



Fig. 1. Molar magnetic susceptibility (χ) vs. temperature for KFeS₂.

Heat capacity measurements were made from 225 to 296 K by differential scanning calorimetry using the Perkin-Elmer DSC-2 calorimeter at a heating rate of $10 \,\mathrm{K \ min^{-1}}$. The accuracy of the measurements is 2-3%. although the precision is an order of magnitude better. Shown in Fig. 2 are the results of two consecutive measurements. Both data sets exhibit a small saw-toothshaped anomaly at $T_N = 254 \pm 2$ K, identical within experimental error to the value of T_N determined from the magnetic susceptibility measurements. The anomaly is characterized by a discontinuity ΔC_p of about 1% $(0.97 \text{ J mole}^{-1} \text{ K}^{-1})$ and by a slope discontinuity, 0.17- $0.078 \text{ J} \text{ mole}^{-1} \text{ K}^{-2}$, upon traversing T_N from below; this behavior is indicative of a weak second order phase transition. However, the value of ΔC_p is only 4.6% of that predicted for long range antiferromagnetic ordering of a spin 5/2 system from the Weiss molecular field approximation; this indicates that extensive short



Fig. 2. Molar heat capacity (C_p) vs. temperature for KFeS₂; the results of two consecutive measurements are shown.

range order persists above T_N , consistent with the magnetic susceptibility results.

Inspection of Figs. 1 and 2 shows that $\chi(T)$ and $C_p(T)$ at and near to T_N are related by a relation proposed by Fisher [26] on general grounds, $C_M \propto \partial(\chi T)/\partial T$, where C_M is the magnetic contribution to the heat capacity. Assuming that the validity of this relation extends to the full temperature range of the $\chi(T)$ measurements, analysis of the $\chi(T)$ and $C_p(T)$ data together yields the Debye temperature $\theta_D \approx 400$ K and the magnetic entropy at T_N , $S_M(T_N) \approx 3.0$ J mole⁻¹ K⁻¹. The latter value is only 20% of the configuration entropy of the high spin Fe³⁺ ion (R ln 6), again indicating the persistance of extensive short-range magnetic order above T_N .

Within the context of known quasi-one-dimensional (1D) antiferromagnets [27], the compound KFeS₂ exhibits 1D magnetic correlations to an unusually high temperature. According to the data of Bronger [3], χ continues to increase nearly linearly with temperature from ~ 370 K up to the chemical decomposition temperature of ~ 700 K, with a slope close to that found here between T_N and 360 K. In the absence of sample decomposition, χ would presumably have shown a broad maximum at a temperature $T^{\max} > 700$ K, followed by an asymptotic approach to a Curie--Weiss behavior.

Neutron diffraction [2, 4] and Mössbauer [6, 8–10] experiments have shown that the low temperature saturation moment (μ^{sat}) in the antiferromagnetically ordered state of KFeS₂ ($\approx 2.4 \mu_B$) is only about half of the value ($5 \mu_B$) expected for high spin Fe³⁺, for which the spin S = 5/2 and the spectroscopic splitting factor g = 2. This depression of μ^{sat} could arise from an Fe³⁺ ground state with a lower effective spin than the value of 5/2 usually assumed [21], from covalent mixing of the Fe³⁺ and sulfur orbitals [8, 9, 12, 28], and/or from the presence of a large zeropoint spin deviation from the classical Néel ground state [27, 29]. The latter is an effect which can be particularly pronounced in 1D antiferromagnets; our χ data indicate that it is important in the case of $KFeS_2$. It appears that these χ data cannot be fitted by theories [27, 30] which do not take zero-point spin deviations into account. This conclusion is most clearly explained by first noting that these theories predict that the ratio $\chi(T^{\max})/\chi(T=0)$ for a powder sample is always less than or equal to the Weiss molecular field value of 1.5; this value is independent of S, g, the number of nearest neighbor magnetic ions, and of the intrachain exchange interaction parameter. In contrast, even after including a diamagnetic core correction of -0.5×10^{-4} cm³ mole⁻¹, the data in Fig. 1 and in [3] together show that this ratio for $KFeS_2$ is at least 2.0. Zero-point spin deviations apparently depress $\chi(T=0)$ significantly below the value it would have had in the absence of spin deviations, and therefore probably also exert a strong influence on the temperature dependence of χ . Further experiments, preferably on single crystals, are necessary to quantitatively establish the relative importance of zero-point spin deviations versus other factors cited above in determining the observed low temperature saturation moment and χ value of KFeS₂.

In conclusion, we have presented a new preparation method for KFeS₂ which yields samples virtually free of paramagnetic and ferromagnetic contaminants; this method would probably also be useful for preparing magnetically pure samples of other $A \operatorname{FeS}_2$ compounds. High precision magnetic susceptibility and heat capacity measurements were carried out on polycrystalline KFeS₂ prepared using the new method, and both measurements exhibited distinct anomalies at the longrange antiferromagnetic transition temperature; these anomalies have not been previously observed. The shapes of the two anomalies were found to be related by the Fisher relation, $C_M \propto \partial(\chi T)/\partial T$. The quasi-onedimensional nature of the magnetic interactions between the iron atoms is clearly manifested in both the susceptibility and heat capacity data at and above T_N .

Acknowledgements – We are grateful to S.P. Frysinger and S.M. Rich for expert technical assistance.

REFERENCES

- 1. J.W. Boon & C.H. MacGillavry, Rec. Trav. Chim. Pays-Bas 61, 910 (1942).
- 2. Z. Tomkowicz, A. Szytula & H. Bak-Ptasiewicz, Phys. Status Solidi (a) 57, K25 (1980).

- 3. W. Bronger, Z. Anorg. Allg. Chem. 359, 225 (1968).
- 4. M. Nishi & Y. Ito, Solid State Commun. 30, 571 (1979).
- 5. E. Fluck, W. Kerler & W. Neuwirth, Angew. Chem. Int. Ed. 2, 277 (1963).
- 6. W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn & B. Zimmermann, Z. Phys. 173, 321 (1963).
- 7. D. Raj & S.P. Puri, *J. Chem. Phys.* 50, 3184 (1969).
- C.A. Taft, D. Raj & J. Danon, J. de Phys. Coll. 35, C6-241 (1974).
- 9. C.A. Taft, D. Raj & J. Danon, J. Phys. Chem. Solids 36, 283 (1975).
- H.P. Nissen & K. Nagorny, Z. Phys. Chem. Neue Folge 95, 301 (1975).
- 11. H.P. Nissen & K. Nagorny, Z. Phys. Chem. Neue Folge 99, 209 (1976).
- 12. C.A. Taft, J. de Phys. 38, 1161 (1977).
- R.B. Scorzelli, C.A. Taft, J. Danon & V.K. Garg, J. Phys. C: Solid State Phys. 11, L397 (1978).
- C.A. Taft, S.F. da Cunha, N.G. de Souza & N.C. Furtado, J. Phys. Chem. Solids 41, 61 (1980).
- T.P. Arsenio, P.H. Domingues & C.A. Taft, *Phys. Status Solidi (b)* 105, K31 (1981).
- T.P. Arsenio, P.H. Domingues, N.C. Furtado & C.A. Taft, Solid State Commun. 38, 205 (1981).
- 17. W.V. Sweeney & R.E. Coffman, *Biochim. Biophys. Acta* 286, 26 (1972).

- R.S. de Biasi & C.A. Taft, J. Mater. Sci. 13, 2274 (1978).
- R.S. de Biasi, C.A. Taft & N.C. Furtado, J. Magn. Magn. Mater. 21, 125 (1980).
- R.S. de Biasi, C.A. Taft & N.C. Furtado, J. Magn. Magn. Mater. 23, 211 (1981).
- 21. W. Bronger & P. Müller, J. Less-Common Metals **70**, 253 (1980).
- 22. C.A. Taft & M.A. de Paoli, Chem. Phys. Lett. 68, 94 (1979).
- 23. J.S. Deutsh & H.B. Jonassen, *Inorganic Syntheses*, Vol. VI. McGraw-Hill, New York (1960).
- 24. A.J. Jacobson, M.S. Whittingham & S.M. Rich, J. Electrochem. Soc. 126, 887 (1979).
- 25. R. Kubo, Phys. Rev. 87, 568 (1952).
- 26. M.E. Fisher, Phil. Mag. 7, 1731 (1962).
- For a review, see L.J. de Jongh & A.R. Miedema, Adv. Phys. 23, 1-260 (1974).
- 28. C.A. Taft & M. Braga, *Phys. Rev.* B21, 5802 (1980).
- For another 1D antiferromagnetic system containing Fe³⁺, see G.P. Gupta, D.P.E. Dickson, C.E. Johnson & B.M. Wanklyn, J. Phys. C10, L459 (1977).
- See, e.g. M.É. Fisher, Am. J. Phys. 32, 343 (1964);
 G.R. Wagner & S.A. Friedberg, Phys. Lett. 9, 11 (1964).