

Neutron-Diffraction Determination of the Antiferromagnetic Structure of KCuF_3 †

M. T. HUTCHINGS, E. J. SAMUELSEN,* AND G. SHIRANE
Brookhaven National Laboratory, Upton, New York 11973

AND

K. HIRAKAWA
Department of Physics, Kyushu University, Fukuoka, Japan
 (Received 25 June 1969)

We have investigated the nuclear and magnetic diffraction of neutrons from powder and single-crystal samples of KCuF_3 at temperatures between 298 and 4.4°K, in order to establish the magnetic structure, and, in particular, to try to determine whether there exist any long-range one-dimensional correlations in this material. Previous work has shown that KCuF_3 has two stable polytype tetragonal structures which may coexist over a large range of temperatures. The samples used in this work indicated the simultaneous presence of both these structures, and gave diffraction peaks indicative of D_{4h}^{18} and D_{4h}^5 space groups. Both structures are found to have type-*A* magnetic ordering with the spins lying in the *a-b* plane. Our results suggest that the D_{4h}^{18} structure orders at $38 \pm 1^\circ\text{K}$, while the D_{4h}^5 may order at $22 \pm 4^\circ\text{K}$. The moment of the Cu^{2+} ion is determined to be $0.49 \pm 0.07 \mu_B$. No direct evidence for one-dimensional order above 38°K nor for long-range one-dimensional correlations has been found, but their presence has not been unambiguously ruled out.

1. INTRODUCTION

THE magnetic properties of the distorted perovskite KCuF_3 have been the subject of a number of recent papers in which some interesting propositions and predictions have been made. Scatturin *et al.*¹ found no evidence of long-range magnetic order above 4.2°K in their neutron-diffraction measurements on powdered KCuF_3 . They suggested the possibility of the existence of one-dimensional linear chains of antiferromagnetically ordered spins along the *c* axis. More recently, Kadota *et al.*² and Hirakawa *et al.*³ have presented data from susceptibility, specific heat, and NMR measurements, which they interpret in terms of a development of one-dimensional antiferromagnetic short-range order below 243°K. They suggest that the particular orbital configuration of the Cu^{2+} ions gives rise to a strong Heisenberg exchange interaction J_c between nearest-neighbor ions along the *c* axis, whereas the interaction between nearest-neighbor ions perpendicular to the *c* axis, J_a , is very small. Using the theory of Bonner and Fisher⁴ and of Oguchi⁵ they estimate $J_c \sim -190^\circ\text{K}$, where $\mathcal{H}_{\text{ex}}^{12} = -2J_c \mathbf{S}^{(1)} \cdot \mathbf{S}^{(2)}$, and $J_a \sim 0.2^\circ\text{K}$. On the other hand, suggestions have been made by both Okazaki and Suemune,⁶ and Hirakawa *et al.*,⁷ that

KCuF_3 should order in a type-*A* pattern, as does LaMnO_3 , a compound with a similar structure and cation orbital wave functions.

The work reported in this paper was undertaken to investigate by elastic neutron scattering the possible existence of long-range one-dimensional correlations, and to establish the low-temperature three-dimensional spin-ordering pattern. One difficulty encountered in this work, as in most of the previous investigations, is the existence of at least two polytype structures belonging to different space groups.

We shall discuss the crystal structure in the next section, and describe the low-temperature neutron measurements in Sec. 3. The measurements are discussed briefly in Sec. 4, and in Sec. 5 we summarize our results.

2. CRYSTAL STRUCTURE

The samples used were small blue crystals and polycrystals of about 36 mm³ volume, prepared in the manner described by Kadota *et al.*² The powder investigated was made by grinding several polycrystals.

The crystal structure of KCuF_3 was first studied in detail by Okazaki and Suemune,⁶ who used x-ray analysis of small shaped single crystals. They found the structure to be tetragonal with probable space group $D_{4h}^{18} - I4/mcm$, with a stacking disorder in the displacement of the fluorine atoms. This structure was found to persist down to at least 78°K with a steady contraction in the lattice constants.⁸ However, one specimen among six investigated by these authors showed weak reflections corresponding approximately to a space group $D_{4h}^5 - P4mbm$. Very recently, Okazaki⁹ has clarified this situation somewhat by further x-ray

† Work performed under the auspices of the U. S. Atomic Energy Commission.

* Guest scientist from Institutt for Atomenergi, Kjeller, Norway.

¹ V. Scatturin, L. Corliss, N. Elliott, and J. Hastings, *Acta Cryst.* **14**, 19 (1961).

² S. Kadota, I. Yamada, S. Yoneyama, and K. Hirakawa, *J. Phys. Soc. Japan* **23**, 751 (1967).

³ K. Hirakawa and S. Kadota, *J. Phys. Soc. Japan* **23**, 756 (1967).

⁴ J. C. Bonner and M. E. Fisher, *Phys. Rev.* **135**, A640 (1964).

⁵ T. Oguchi, *Phys. Rev.* **133**, A1098 (1964); M. E. Lines (private communication).

⁶ A. Okazaki and Y. Suemune, *J. Phys. Soc. Japan* **16**, 176 (1961).

⁷ K. Hirakawa, K. Hirakawa, and T. Hashimoto, *J. Phys. Soc. Japan* **15**, 2063 (1960).

⁸ A. Okazaki and Y. Suemune, *J. Phys. Soc. Japan* **16**, 671 (1961).

⁹ A. Okazaki, *J. Phys. Soc. Japan* **26**, 870 (1969); **27**, 518 (1969).

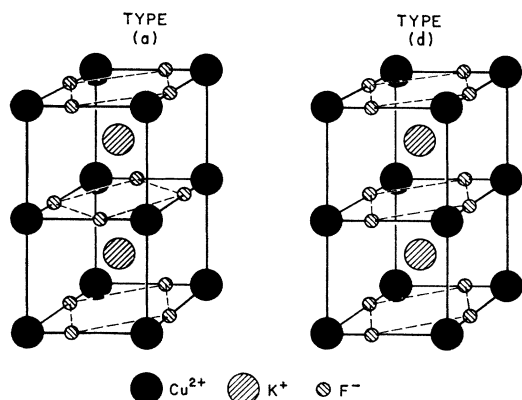


FIG. 1. Schematic structure of types (a) and (d) observed by Okazaki (Ref. 9).

work in which he has found evidence for two polytype structures of KCuF_3 , both with and without stacking disorders. Their exact space groups, however, remain ambiguous. His results are summarized in Table I and Fig. 1. Both structures appear to be stable over a wide range of temperatures; it is not clear under what conditions of growth each is formed.

The two structures proposed by Okazaki (Fig. 1) both represent distortions from the ideal perovskite structure. The distortion is attributed to a cooperative Jahn-Teller effect.¹⁰ In each structure the fluorines are displaced from the midpoint of the Cu^{2+} - Cu^{2+} bonds in a manner which may be thought of as a small rotation of the F^- ions about the c axis. In one (types a and b) the sense of the rotation alternates up the c axis, whereas in the other (types c and d) the rotation is always in the same sense. We shall refer to these as probable D_{4h}^{18} and D_{4h}^5 space groups, respectively. The distortions give rise to superstructure peaks in addition to the ideal perovskite diffraction peaks. In each of the structures a one-dimensional ordering arising through the mechanism proposed by Kadota *et al.* is possible.

The present neutron measurements, described below, also indicate the existence of at least two forms of KCuF_3 ; however, they suggest they may coexist in the same crystal sample. In general, a given crystal even of one space group has a multidomain structure corresponding to the three possible directions of the c axis.

TABLE I. Two polytype structures of KCuF_3 .^a

Type	Tetragonal cell constants	Pseudo cubic cell constants	Stacking disorder	a_0 (Å)	c_0 (Å)
a	$a = \sqrt{2}a_0$ $c = 2c_0$	$2a_0$ $2c_0$	No	4.1410 ± 2	3.9237 ± 2
b	$a = \sqrt{2}a_0$ $c = 2c_0$	$2a_0$ $2c_0$	Yes		
c	$a = \sqrt{2}a_0$ $c = c_0$	$2a_0$ c_0	Yes		
d	$a = \sqrt{2}a_0$ $c = c_0$	$2a_0$ c_0	No	4.1396 ± 2	3.9303 ± 5

^a Reference 9.

¹⁰ J. Kanamori, J. Appl. Phys. 31, 14S (1960).

TABLE II. Conditions for diffraction referred to a pseudo perovskite cell of sides $2a_0$, $2a_0$, and $2c_0$.

Space group	Condition
D_{4h}^{18}	(i) (hkl) all even
	or
D_{4h}^5	(ii) (hkl) all odd, but not (hhl)
	or
D_{4h}^{13}	(i) (hkl) all even
	or
D_{4h}^{13}	(ii) h and k even, l odd, but not h or $k=0$
	h and k odd, l odd or even, but not (hhl)

It is possible to find crystals in which one domain predominates; two such crystals were chosen for the neutron measurements. Since these showed somewhat different diffraction patterns, we shall refer to them as samples I and II.

Both crystals used were imperfect. Sample I was $\sim 96\%$ single domain and showed multicrystalline growth with a mosaic spread of $\sim 1^\circ$, each Bragg reflection consisting of two or three peaks. Sample II had a narrower mosaic of $\sim 0.4^\circ$, again with some peak splitting, and was $\sim 93\%$ single domain. Although a single domain could be singled out for investigation, the relatively large orientational spreads precluded accurate intensity measurements.

All the neutron measurements were made with incident neutrons of wavelength 1.447 Å. Powder diffraction patterns were taken at 296, 78, and 4.2°K, and diffraction from both crystals was investigated at 296°K and at temperatures between 4.2 and 70°K. We shall discuss the nuclear scattering below and the magnetic scattering, observed at lower temperatures, in Sec. 3.

The nuclear peaks were investigated with a view to obtaining information on the space group rather than on detailed structure parameters for the crystals used. In Table II, we list the conditions for observation of peaks from the tetragonal space groups D_{4h}^{18} , D_{4h}^5 , and D_{4h}^{13} . The indices are referred to the pseudoperovskite fundamental cell of sides $(2a_0, 2a_0, 2c_0)$ in each case; we shall adopt this as our reference cell throughout this paper. The upper rule (i) is the ideal perovskite condition, and the lower one (ii) the condition for observation of superstructure lines due to the displacement of the fluorine atoms.

Of the nuclear peaks detected, the (131), (313), and (310) peaks were observed in both samples I and II. These indicate the presence of both D_{4h}^{18} and D_{4h}^5 space groups, respectively. However, the (310) was relatively much weaker in sample I. Although the simultaneous presence of these peaks is consistent with a D_{4h}^{13} space group, the fact that the relative intensities of the peaks varied from sample to sample indicates that each is a mixture of D_{4h}^{18} and D_{4h}^5 , sample I being

TABLE III. Observed and calculated relative intensities for the magnetic peaks in sample I.

Peak	I_{obs}	I_{calc}
(001) M^a	188	181
(003) M^a	43	42
(005) M^a	13	13
(221) M	20	26
(223) M	15	18
(002) N^a	4480	4330
(004) N^a	11 800	19 200
(222) N	4401	4290

^a Average experimental intensity of (00 l) and (00 \bar{l}).

predominantly D_{4h} ¹⁸. The powder data indicated that there too both space groups were present, the (131), (310), and (312) peaks being observed. In the earlier powder diffraction work by Scatturin *et al.*, superstructure peaks at the nearly coincident (310)-(301), and (312)-(213) positions were also seen. They further observed a small (111) peak which we have not found in any sample. This was very probably due to $\frac{1}{2}\lambda$ contamination which was absent in our measurements due to the use of a germanium (311) plane as monochromator.

Powder x-ray patterns were made on all three samples in order to check their lattice spacing. In each case, values of $a_0=4.140\pm 0.001$ Å and $c_0=3.925\pm 0.001$ Å were obtained. These are close to Okazaki's values for type a (Table I).

3. MAGNETIC STRUCTURE

On cooling to 4.2°K, the powder sample showed additional small magnetic peaks at angles corresponding to the {001} and {201} reciprocal lattice points. These suggest a type-A ordering pattern of the spins; that is, ferromagnetic sheets in the a - b plane antiferromagnetically stacked up the c axis, giving a tetragonal magnetic unit cell with sides of length ($a_0, a_0, 2c_0$). This structure was confirmed on examining the single crystals, and in Tables III and IV we summarize the results of integrated intensity measurements at 4.2°K and calculated intensities for the two samples. The magnetic peaks observed all had h and k even and l odd. Where possible, averages of peaks with opposite τ vectors were taken to compensate for the poor crystal quality. The intensities of the nuclear peaks given in the tables, which are main perovskite peaks, were calculated assuming an ideal perovskite lattice. The magnetic peaks were related to the nuclear peaks using only the {001} M and {002} N peak intensities to minimize the effects of the mosaic spread. In calculating the intensities, the scattering lengths taken were $K=0.37$,¹¹ $\text{Cu}=0.79$,¹² and $F=0.55$,¹³ and the cal-

¹¹ G. E. Bacon and J. S. Plant, *Z. Krist.* **126**, 460 (1968).

¹² D. T. Keating, W. J. Neidhardt, and A. N. Goland, *Phys. Rev.* **111**, 261 (1958).

¹³ C. G. Shull and E. O. Wollan, *Phys. Rev.* **81**, 527 (1951).

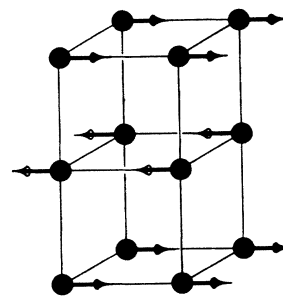


FIG. 2. Magnetic structure of KCuF_3 . The directions of the spins in the a - b plane is not determined.

TYPE A MAGNETIC STRUCTURE

culated Cu^{2+} form factor¹⁴ was used. Satisfactory agreement between calculated and observed intensities could only be obtained if the spins lay in the a - b plane. However, the direction in this plane remains unknown. The magnetic structure is illustrated in Fig. 2. The lattice constants for both crystals at 4.4°K determined by neutron scattering, $a_0=4.115\pm 0.003$ Å and $c_0=3.907\pm 0.004$ Å, are in good agreement with the results of Okazaki and Suemune.⁸

The magnetic moment of the Cu^{2+} ion at 4.4°K was found from the ratio of intensities of the innermost magnetic peaks (001) M and (00 $\bar{1}$) M , and nuclear peaks (002) N and (00 $\bar{2}$) N , using the calculated form factor $f(001)=0.975$. For sample I, we find $\mu=0.54\pm 0.04$ μ_B , and sample II $\mu=0.46\pm 0.09$ μ_B . The moment was also estimated from the powder data using the ratio of the integrated intensity of (001) M peak and a weighted average of the (002) N and (200) N peaks, giving a value of $\mu=0.48\pm 0.05$ μ_B . These values are calculated assuming complete stoichiometry, for which we cannot test directly. However, the fact that they internally agree appears to support the assumption.

The temperature variation of the integrated intensity of the (001) M and (221) M peaks in sample I is shown in Fig. 3. T_N is found to be 38 ± 1 °K. The intensities of the two peaks are normalized to coincide at 4.4°K, and the temperature variation of the two peaks agrees

TABLE IV. Observed and calculated relative intensities for the magnetic peaks in sample II.

Peak	I_{obs}	I_{calc}
(001) M	611	603
(003) M	156	138
(005) M	52	42
(201) M	116	142
(203) M	75	87
(205) M	31	34
(401) M	48	43
(403) M	31	32
(002) N	20	19

¹⁴ H. Umebayashi, B. C. Frazer, D. E. Cox, and G. Shirane, *Phys. Rev.* **167**, 519 (1968).

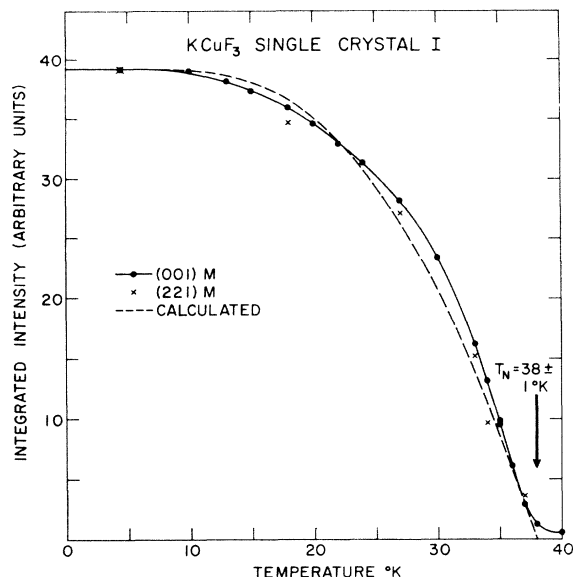


FIG. 3. Temperature variation of the sublattice magnetization in sample I.

within the experimental errors indicating that spin direction does not change. Also shown in Fig. 3 is the square of the sublattice magnetization M^2 , calculated on the molecular-field model by numerically solving the equation

$$\frac{M}{M_0} = B_{1/2} \left(\frac{T_N M}{T M_0} \right),$$

where $B_{1/2}$ is the $S = \frac{1}{2}$ Brillouin function and M_0 is the magnetization as $T \rightarrow 0^\circ\text{K}$. It is seen that there is generally good agreement with experiment but deviations are seen near $T=0$ and T_N , where the molecular field theory is expected to be a poor approximation.

The temperature variation of the integrated intensity of the (001) M and (201) M peaks in sample II is shown in Fig. 4. Although both peaks follow the same curve within the estimated experimental errors, it is at once seen that the variation is quite anomalous. Although the magnetization again vanishes at $38.5 \pm 1.0^\circ\text{K}$, it appears to have two components at lower temperatures. The calculated squared sublattice magnetization shown in Fig. 4 is the sum of two curves determined from the above formula, the values of M_0 have been adjusted to give the total observed intensity at 4.4°K , and the Néel temperatures of 22 and 38°K are found from an approximate fit to the observed points. Also plotted is the variation of the powder (001) M peak intensity, normalized at 4.4°K , which again shows an anomalous rise, this time below 10°K . The peak persists somewhat above 38°K .

In view of the relative intensities of the nuclear superstructure peaks in the two crystal samples, it is tempting to attribute 38°K as the Néel point of KCuF_3 with the D_{4h}^{18} probable space group, and $\sim 22^\circ\text{K}$

that of KCuF_3 with the D_{4h}^5 probable space group. However, as in the case of the nuclear structure, further work is needed on single-structure samples to confirm this conjecture. The powder data, which is clearly not explained on this hypothesis, remains ambiguous. All magnetic phases, however, indicate a type- A ordering with the spins in the a - b plane, and a small magnetic moment of $\sim 0.5 \mu_B$.

If there were one-dimensional order, or long-range correlations above T_N , we would expect to observe a plane, or pancake, of elastic intensity in reciprocal space instead of the usual Bragg spot. For antiferromagnetic ordering along the c axis, these planes would be perpendicular to the c direction and have the form (x, y, l) , where l is odd. We have made a careful search for such a plane or pancake in the region of the (001) M and (201) M reciprocal-lattice points at 42, 50, and 4.2°K using sample II, but have observed no indication of one. Indeed, away from the reciprocal-lattice points the intensities at all three temperatures were very similar. Rough calculations indicate that if we had had perfect one-dimensional order, the intensity observed scanning perpendicular to the reciprocal-lattice plane would be $\sim 10^{-3}$ - 10^{-4} of that of the (001) M peak. We estimate that we could detect the presence of intensity down to $\sim 5 \times 10^{-4}$ of that of the (001) M peak, which gave 6×10^4 counts in 100 sec. Since this is above the lower limit of the estimated expected intensity, we cannot unambiguously rule out the presence of long-range one-dimensional correlations from our measurements. We shall discuss the indirect evidence for and against one-dimensional order below.

4. DISCUSSION

In the absence of any positive evidence from the neutron measurements for the existence of one-dimensional correlations, we cannot confirm directly the model of Kadota *et al.*² for temperatures above 38°K . However, it seems difficult to explain the broad peak observed in the susceptibility curve at 243°K ,⁷ on any other model, although the implied magnitude of J_c , $\sim -190^\circ\text{K}$, is much greater than expected from the other perovskite fluorides. The corresponding interaction is -3.8 ,¹⁵ -10 ,¹⁶ and -45°K ,¹⁷ respectively, for KMnF_3 , KCoF_3 , and KNiF_3 . Taking $T_N = 38^\circ\text{K}$ for the temperature of three-dimensional order, Oguchi's theory⁵ gives $0.05 > |J_a/J_c| > 0.01$, which is more plausible than the earlier estimate of < 0.001 for this ratio.²

¹⁵ S. J. Pickart, M. F. Collins, and C. G. Windsor, *J. Appl. Phys.* **37**, 1054 (1966).

¹⁶ W. J. L. Buyers, R. A. Cowley, T. M. Holden, E. C. Svensson, M. T. Hutchings, D. Hukin, and R. W. H. Stevenson, in *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, Scotland, 1968*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (University of St. Andrews Printing Department, St. Andrews, Scotland, 1969), p. 1330.

¹⁷ M. E. Lines, *Phys. Rev.* **164**, 736 (1967).

Other possible causes of the susceptibility peak should be considered. One possibility is the presence of impurities. However, the reproducibility seems to rule this out, although one sample reported shows no peak.² Another possibility which suggests itself is the effect of the splitting of the lowest 2E orbital doublet in the distorted octahedral crystal field. However, as the orbital moment operator has no matrix elements within the manifold of 2E states, the g values of both states will differ only slightly from the spin-only value of 2.0. This difference will arise through admixtures of the upper crystal-field levels by the distortion field and spin-orbit coupling. The measured g values of the lower doublet are $g_n = 2.27$ and $g_e = 2.14$,² and similar values would be expected for the upper doublet. Any temperature population effect of such levels will modify the susceptibility only slightly. Indeed, calculations obtained by use of an isotropic model show that only if the upper level at $\sim 240^\circ\text{K}$ has a g value of more than twice that of the lower level will the susceptibility show a peak. We are therefore led to conclude that this is not likely to be the cause of the broad maximum.

The small magnitude of the observed Cu^{2+} ion moment, $\sim 0.5 \mu_B$, is perhaps a surprising result, but may be accounted for if $J_a \ll J_c$. The moment measured by neutron diffraction will be reduced from the value $g \mu_B S = 1.1 \mu_B$ by two principal effects: covalency¹⁸ and zero-point spin deviations.¹⁹ The covalency reduction is estimated to be $\sim (10 \pm 6)\%$, leaving the remaining discrepancy to be accounted for by the zero-point spin deviation. In a simple cubic type- G antiferromagnetic, this reduction would only amount to a further 16%.¹⁹ But in type- A structure any tendency for the antiferromagnetic coupling along the c axis to predominate will increase the deviation rapidly. Lines²⁰ has calculated that a 40% reduction may arise if $|J_a/J_c| \sim 0.1$. The low value of our measured moment thus seems consistent with the fact that J_c is larger than J_a , and the order of magnitude appears to be consistent with the estimate of the ratio of exchange constants made, assuming a one-dimensional order, from T_N and the susceptibility maximum.

5. SUMMARY

We have investigated the magnetic structure of two single crystals and a powder of KCuF_3 . All show type- A ordering with the spins lying in the a - b plane. One crystal, which appeared to be composed of mainly one

¹⁸ J. Hubbard and W. Marshall, Proc. Phys. Soc. (London) **86**, 561 (1965).

¹⁹ P. W. Anderson, Phys. Rev. **86**, 694 (1952).

²⁰ M. E. Lines (private communication). Although simple spin-wave theory breaks down for very small values of $|J_a/J_c|$, calculations based on spin-wave theory may be taken to indicate the trend of the deviation with this ratio.

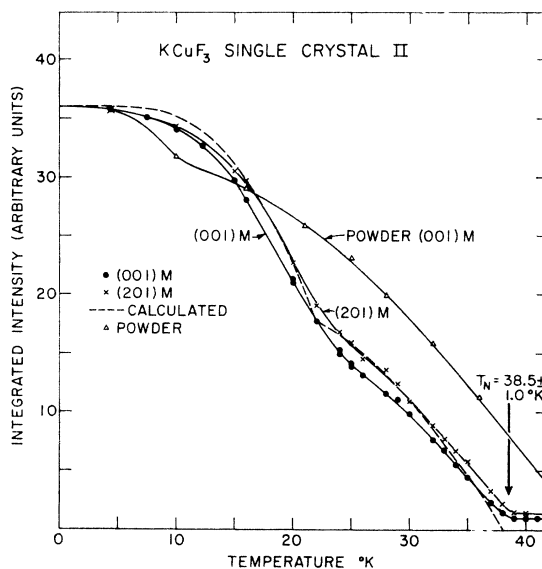


FIG. 4. Temperature variation of the sublattice magnetization in sample II and the powder sample.

polytype structure with probable space group D_{4h}^{18} had a Néel temperature of $38 \pm 1^\circ\text{K}$. The other appeared to be composed of two probable structures D_{4h}^{18} and D_{4h}^5 . It showed an anomalous temperature variation of magnetization suggesting that the two structures may have different Néel temperatures, so that of D_{4h}^5 is $\sim 22^\circ \pm 4^\circ\text{K}$. The powder also showed an anomalous magnetization variation, the origin of which is not clear. The moment at 4.4°K given by the three samples is $0.49 \pm 0.07 \mu_B$, and indicates a large zero-point spin deviation effect. Refinement of these results must await the availability of perfect crystals of one structure.

No direct evidence for long-range correlations in one dimension was obtained from the neutron results, but their presence above 38°K could not be unambiguously ruled out. The indirect evidence for one-dimensional behavior has been discussed. Although there is indication that J_a/J_c is small, the most puzzling aspect remains the requirement of a relatively very large ($\sim 190^\circ\text{K}$) interaction between ions along the c axis.

ACKNOWLEDGMENTS

One of us (E. J. S.) is grateful for a fellowship from Norges Teknisk-Naturvitenskapelige Forskningsråd, Oslo. We would like to thank A. Okazaki for communicating his results prior to publication, and Y. Kuroki for help in the growth of the crystals. We wish to acknowledge useful discussions with M. Blume and M. E. Lines. We are grateful to F. Thomsen for assistance with the cryogenics, and to J. Hurst for running the powder x-ray diffraction photographs.