

Magnetic and specific heat studies of the cation-ordered pyrochlore $\text{NH}_4\text{CoAlF}_6$

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The cation-ordered form of the pyrochlore related fluoride $\text{NH}_4\text{CoAlF}_6$ has been studied with respect to the magnetic susceptibility and specific heat. Susceptibility and magnetization studies indicate Curie-Weiss behavior above about 60 K with an effective moment of $5.70(1)\mu_B/\text{Co}^{2+}$ and $\theta_p = -62(1)$ K. Evidence for magnetic ordering is seen below about 6 K, and the field-cooled-zero-field-cooled susceptibilities, measured at an applied field of 100 G, deviate below 5 K. A substantial ferromagnetic moment of $0.4\mu_B/\text{Co}^{2+}$ is found at 2 K in the magnetization. The specific heat data indicate a remarkably complex behavior with three transitions at 0.8, 2.5, and 5.8 K, the highest and lowest being also observed in the magnetic measurements. Furthermore, short-range correlations are also evident from the presence of a broad peak centered at about 9 K and a considerable excess specific heat contribution extending up to higher temperatures. In fact, 50% of the total observed entropy removal occurs between 25 and 5.8 K. The magnetic specific heat data above 6 K are in good agreement with the one-dimensional $S = \frac{1}{2}XY$ model which is consistent with the chain structure of the Co^{2+} sublattice in ordered $\text{NH}_4\text{CoAlF}_6$. [S0163-1829(98)02634-4]

I. INTRODUCTION

Recently, there has been a wide variety of studies on magnetically frustrated pyrochlore materials which exhibit spin-glass-like behavior without having any apparent site disorder (Refs. 1 and 2 and references therein). Pyrochlore materials with a general formula $R_2M_2O_7$, where R = rare-earth metal and $M = 3d$ or $4d$ transition metal, are described in the space group $Fd\bar{3}m$ with R in $16d$, M in $16c$, $O(1)$ in $48f$, and $O(2)$ in $8b$.³ Both metal atoms, separately, form a three-dimensional network of corner-sharing tetrahedra. The presence of nearest-neighbor antiferromagnetic exchange interactions on such a lattice leads to a high degree of magnetic frustration. Pyrochlores belonging to the $R_2\text{Mo}_2\text{O}_7$ and $R_2\text{Mn}_2\text{O}_7$ series exhibit interesting magnetic phenomena varying from spin-glass to complex magnetic long-range ordering.^{1,2}

Fluoride pyrochlores of the type $\text{NH}_4\text{MM}'\text{F}_6$ have also been studied.⁴ Here the large NH_4^+ ion occupies the $8a$ site, the $16d$ site is empty, the $16c$ site is occupied by M and M' , F is in $48f$, and the $8b$ site is vacant. There are two possibilities, randomness or order between the M and M' ions.

In the case of disordered M and M' , the $Fd\bar{3}m$ symmetry of the cubic pyrochlore is retained and M and M' occupy randomly the $16c$ position. Cation-disordered $\text{AMM}'\text{F}_6$ pyrochlores such as CsMnFeF_6 generally show magnetic behavior which is spin-glass related with no long-range order due to the combination of geometric frustration and random exchange interactions.⁵

For cation-ordered materials a crystallographic distortion occurs to $Pnma$ symmetry. Only a few such cases are known

such as $\text{NH}_4\text{Fe}_2\text{F}_6$ and, recently, $\text{NH}_4\text{CoAlF}_6$.^{4,6} In these compounds M and M' form distinct sublattices consisting of chains which run parallel to $[100]$ and $[010]$ of the orthorhombic cell as shown in Fig. 1. Thus the geometric frustration inherent in the pyrochlore is at least partially alleviated.⁷ Ordered $\text{NH}_4\text{Fe}^{2+}\text{Fe}^{3+}\text{F}_6$, for example, shows a complex canted antiferromagnetic long-range order rather than spin glassiness.⁸ In this case, of course, both Fe^{2+} and Fe^{3+} are magnetic and the two chains interact strongly. To date there have been no studies of cation-ordered pyrochlores in which

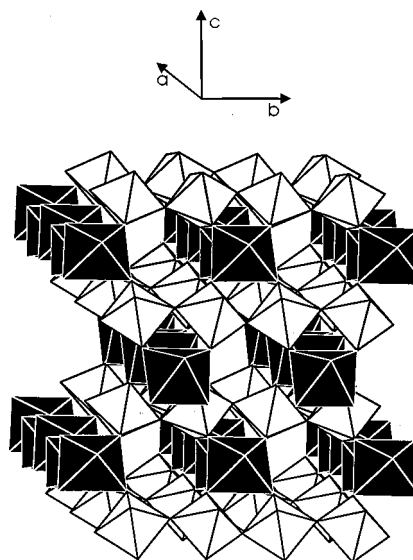


FIG. 1. Perspective view of $\text{NH}_4\text{CoAlF}_6$. The black shaded and unshaded octahedra represent the Co^{2+} and Al^{3+} environments, respectively.

only one sublattice is magnetic. In such cases the geometric frustration is further reduced, and in addition the magnetic chain tendencies are enhanced due to isolation by the connecting diamagnetic chains. To investigate the consequences of cation ordering between magnetic and nonmagnetic M and M' in an $AMM'F_6$ system, the material $\text{NH}_4\text{CoAlF}_6$ has been studied.

II. EXPERIMENT

A. Sample preparation

Sample preparation and structural analysis have been reported in Ref. 6. X-ray powder diffraction indicates that the compound is orthorhombic with lattice constants $a = 7.134 \text{ \AA}$, $b = 7.052 \text{ \AA}$, and $c = 9.930 \text{ \AA}$.

B. Magnetic studies

Zero-field-cooled (ZFC) and field-cooled (FC) dc magnetic susceptibilities in the temperature range 2–300 K and magnetization up to an applied field of 5.5 T were measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design, San Diego). The ac susceptibility χ' was measured in zero external magnetic field at a frequency of 133 Hz by the mutual inductance method. The primary coils of the mutual inductor are energized by a frequency generator (DS 335, Stanford Research Systems). The output across the two identical secondary coils, wound in opposite directions, was measured using a lock-in amplifier (SR-830 DSP, Stanford Research Systems). The sample's susceptibility was obtained from the difference in the outputs with the sample in the middle of the top secondary coil and without the sample. The cryostat used for the temperature variation is described in the section below.

C. Specific heat

The specific heat of the sample in the form of a pellet ($\sim 100 \text{ mg}$) was measured in the temperature range 0.3–25 K using a quasiadiabatic calorimeter and a commercial Heliox sorption pumped ^3He cryostat supplied by Oxford Instruments. The sample was mounted on a thin sapphire plate with apiezon for better thermal contact. Underneath the sapphire plate a strain gauge heater and a RuO_2 temperature sensor were attached with G-E varnish. The temperature of the calorimetric cell was controlled from the ^3He pot on the heliox. The sample temperature was measured using an LR-700 ac resistance bridge at a frequency of 16 Hz. The specific heat of the sample was obtained by subtracting the contribution of the addendum, measured separately, from the total measured heat capacity.

III. RESULTS AND DISCUSSION

A. Magnetic data

Zero-field-cooled and field-cooled susceptibilities of $\text{NH}_4\text{CoAlF}_6$, measured at an applied field of 100 G, are shown as a function of temperature below 20 K in Fig. 2(a). A magnetic ordering at about 6 K is observed by a sharp rise in the susceptibility. The divergence of ZFC and FC curves below 5 K is also clear. However, this divergence is only representative for the susceptibilities measured at an applied

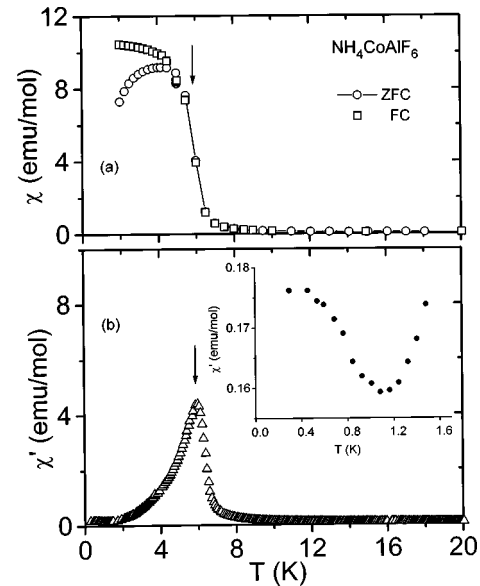


FIG. 2. (a) Zero-field-cooled (ZFC) and field-cooled (FC) dc susceptibilities for $\text{NH}_4\text{CoAlF}_6$. (b) ac susceptibility χ' against temperature. Inset shows the same plot on an expanded scale.

field of 100 G as the magnetization, which will be seen later becomes strongly nonlinear at low temperatures.

Since the temperatures below 2 K are out of range of the SQUID magnetometer used in the present studies, the ac susceptibility χ' was measured down to 0.3 K. Here χ' , measured in zero external magnetic field at a frequency of 133 Hz, is plotted against temperature in Fig. 2(b). No attempt was made to study the effects of frequency and external magnetic field on χ' as the main objective here is to look for possible magnetic anomalies down to 0.3 K. Here χ' rises sharply below about 7 K and shows a sharp peak at slightly below 6 K coinciding with the inflection point in the dc susceptibility curve. Below 6 K the χ' continues to decrease with decreasing temperature, but below 1 K a weak upturn is found. This is difficult to see in Fig. 2(b), but the expanded version of the same plot in the inset clearly shows a sharp rise in χ' with an inflection point close to 0.8 K.

The inverse susceptibility versus temperature follows Curie-Weiss behavior above 60 K as shown in Fig. 3. The Curie constant C obtained from the Curie-Weiss fit corresponds to $5.70(1) \mu_B / \text{Co}^{2+}$, which is within the range for Co^{2+} ions. The paramagnetic Curie temperature θ_p , of

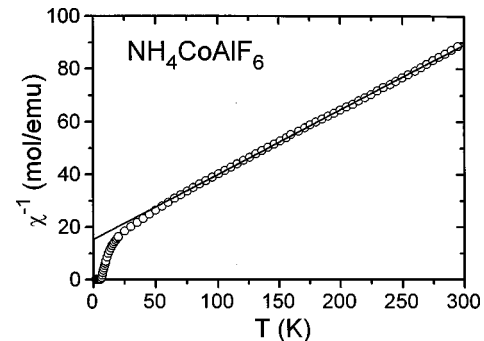


FIG. 3. Inverse molar susceptibility against temperature for $\text{NH}_4\text{CoAlF}_6$. The solid line represents Curie-Weiss behavior.

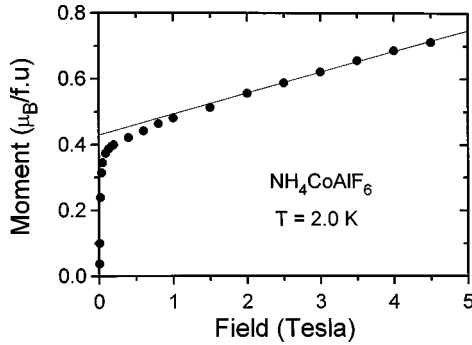


FIG. 4. Magnetization as a function of applied magnetic field for $\text{NH}_4\text{CoAlF}_6$.

$-62(1)$ K is indicative of predominant antiferromagnetic interactions. The $|\theta_p|/T_c \sim 10$ is large and indicates that the system encounters difficulty in finding a magnetic ground state.

Magnetization against an applied field at 2.0 K is plotted in Fig. 4. The magnetization increases very steeply up to about 0.2 T, above which a gradual, linear increase occurs. A linear extrapolation to zero field of the magnetization data at higher fields gives a saturation moment of $0.43\mu_B/\text{Co}$. Magnetization at higher fields continues to increase at a rate of $0.064\mu_B/\text{Co}/\text{T}$. The saturation magnetization behavior at low applied fields and the sharp rise in the susceptibility below the T_c clearly suggest the presence of a ferromagnetic component to the ordered state, due possibly to an extreme sublattice canting.

B. Specific heat

The specific heat of the pelletized powder sample of $\text{NH}_4\text{CoAlF}_6$ versus temperature is shown in Fig. 5(a) between 0.3 and 25 K. This plot shows three sharp specific heat anomalies at 5.8, 2.5, and 0.8 K. While the specific heat anomaly at about 5.8 K has corresponding magnetic anomalies in the ac and dc susceptibilities, that for the peak at 2.5 K appears to be buried under the very large anomaly in χ' centering at 5.9 K. Below 2 K only ac susceptibility data are available, which show an anomaly close to 0.8 K as explained earlier. The solid line in Fig. 5(a) represents the estimated lattice specific heat of the sample. This contribution was obtained by measuring the specific heat of a nonmagnetic isostructural compound $\text{NH}_4\text{ZnAlF}_6$ and following the scaling procedure as described in Ref. 9. The magnetic specific heat C_m obtained by subtracting the lattice contribution from the total measured specific heat C_p exhibits, apart from the three sharp peaks, a broad anomaly with a maximum at about 9 K and extending to much higher temperatures at least to $\sim 5T_c$. While the three λ -type anomalies at 5.8, 2.5, and 0.8 K appear to be due to long-range magnetic ordering, the broad anomaly indicates the presence of short-range spin-spin correlations at higher temperatures.

The magnetic entropy S_m as a function of temperature is obtained by numerically integrating the C_m/T data using the thermodynamic relationship

$$S_m(T) = \int_0^T \frac{C_m}{T} dT$$

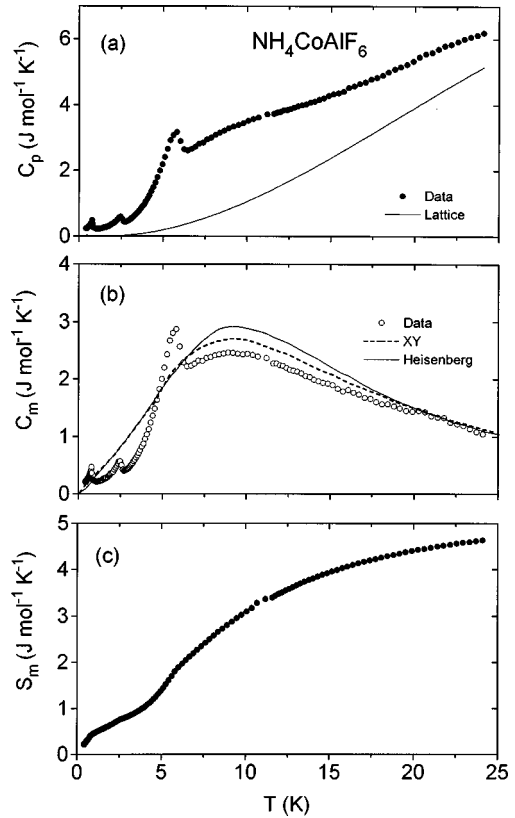


FIG. 5. (a) Measured specific heat C_p of $\text{NH}_4\text{CoAlF}_6$ (solid line corresponds to the estimated lattice specific heat), (b) experimental and theoretical magnetic specific heat C_m , and (c) magnetic entropy S_m against temperature.

and is plotted in Fig. 5(c). The C_m data below 0.3 K were extrapolated linearly to 0 K to estimate the remaining entropy, which is about $0.2 \text{ J mol}^{-1} \text{ K}^{-1}$. This value, in any case, does not significantly alter the entropy of $4.6 \text{ J mol}^{-1} \text{ K}^{-1}$ reached at 25 K. However, it should be mentioned that there is a total error of about 5% in determining the lattice specific heat of $\text{NH}_4\text{CoAlF}_6$ due to the error in the absolute measurement of the nonmagnetic compound $\text{NH}_4\text{ZnAlF}_6$ and a possible error in the scaling procedure. The maximum entropy expected for a two-level system is $R \ln(2) = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}$ (a ground doublet seems appropriate to assume as Co^{2+} is a Kramers ion). With increasing temperature, the entropy value reached at the 5.8 K transition is about $1.8 \text{ J mol}^{-1} \text{ K}^{-1}$, which is only 31% of the total expected entropy. The value of $4.6 \text{ J mol}^{-1} \text{ K}^{-1}$ reached at the maximum temperature in the present studies is 80% of the expected entropy. It appears that the remaining entropy exists at temperatures above 25 K due, presumably, to short-range ordering, assuming that the entropy estimated below 0.3 K is correct.

In the Introduction, it was mentioned that Co^{2+} and Al^{3+} form linear chains in the [100] and [010] directions, respectively. Since long-range ordering is not possible as long as the magnetic interactions are confined to one dimension, the entropy for such a system is due to short-range ordering only. The observed values of C_m above 6 K in Fig. 5(b), upon comparison with the numerically calculated values for different $S = \frac{1}{2}$ models (i.e., Ising, XY, and Heisenberg spins on one-dimensional lattice), are found to be closest to the

values for the antiferromagnetic XY model. The numerically calculated values are taken for one-dimensional (1D) XY and Heisenberg models from Ref. 10, and the exchange parameter $|J|/k_B$ was adjusted to match the maxima of the experimental data and the model curves as shown in Fig. 5(b). The values of exchange parameter $|J|/k_B$ for XY and Heisenberg models are 14.5 and 10.0 K, respectively. The close agreement between the experimental and theoretical C_m behaviors suggests that the short-range 1D behavior is effective down to 6 K, below which interchain interactions become operative and lead to a long-range order as indicated by the sharp anomaly in the C_m . The other two sharp anomalies in the C_m data at 2.5 and 0.8 K appear to be more likely due to magnetic transitions as the structural distortions, which also could give rise to the specific heat anomalies, are less likely to take place at such low temperatures.

In summary, the specific heat studies provide evidence for three possible long-range magnetic orderings at 0.8, 2.3, and 5.8 K and, above that, a short-range ordering. The short-

range order is well described by the one-dimensional XY model for $S = \frac{1}{2}$ and is consistent with the crystal structure which features relatively isolated linear chains of Co^{2+} . Magnetic susceptibility and magnetization data indicate predominant antiferromagnetic interactions, but also a rather large ferromagnetic component in the ordered state. In order to provide conclusive evidence for the existence of the short-range spin-spin correlations and to determine the magnetic structures at low temperatures, neutron diffraction studies are needed. However, the presence of hydrogen in $\text{NH}_4\text{CoAlF}_6$ precludes neutron studies unless hydrogen can be replaced with deuterium, and our efforts are in that direction.

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