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MAGNETIC TRANSITIONS IN $\text{NiBr}_2 \cdot 6\text{NH}_3$ AND $\text{NiCl}_2 \cdot 6\text{NH}_3$
UP TO 75 kOe *

by

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ABSTRACT

The field dependence of the magnetic susceptibility of powdered $\text{NiBr}_2 \cdot 6\text{NH}_3$ and $\text{NiCl}_2 \cdot 6\text{NH}_3$ was measured up to 75 kOe at temperatures above and below T_N . The anomalies found are discussed in terms of other magnetic data known for these salts.

RESUMO

A dependência da susceptibilidade magnética com o campo magnético de amostras em pó de $\text{NiBr}_2 \cdot 6\text{NH}_3$ e $\text{NiCl}_2 \cdot 6\text{NH}_3$ foi medida até 75 kOe em temperaturas abaixo de T_N . As anomalias encontradas são discutidas em termos dos demais dados magnéticos conhecidos para estes sais.

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The Nickel Hexamine Halides are cubic salts in which the Ni^{++} ions form an f.c.c. lattice¹. The six NH_3 molecules are disposed in the vertices of an octahedron around each Ni^{++} , and are primarily responsible for the crystalline field acting on them. The average symmetry of this crystalline field depends on the rotational state of the NH_3 molecules. Above a certain temperature (76 K for the Chloride, 40 K for the Bromide and 20 K for the Iodide) this average symmetry is cubic, but below it is trigonally distorted²⁻⁴. From EPR data, the splitting of the Ni^{++} ground triplet caused by this distortion was determined to be $D \approx 0.3 \text{ cm}^{-1}$ ($D/k \sim 0.4 \text{ K}$) for all the halides⁵. Specific heat measurements indicated an antiferromagnetic transition at $T_N = 1.0 - 1.4 \text{ K}$ for the Chloride (the data shows two distinct peaks), at $T_N = 0.6 \text{ K}$ for the Bromide and at $T_N = 0.3 \text{ K}$ for the Iodide⁶. However, the temperature dependence of the zero-field magnetic susceptibility, measured down to 0.3 K, did not show the expected behavior for an antiferromagnet⁷. The ratio θ/T_N also (θ being the Weiss temperature) was found to be quite high, of the order of 10 for all the halides⁷.

In this paper we report measurements of the magnetic field (H) dependence, up to 75 kOe, of the magnetic susceptibility (χ) on powdered samples of the Bromide and Chloride above and below T_N . Since our lowest attainable temperature was 0.3 K, we could not reach below T_N for the Iodide. We hoped to establish the

magnetic phase diagram for these salts. The field dependence of the magnetic susceptibility has been measured in other cubic, low anisotropy, antiferromagnets and it shows conspicuously the spin-flop and the canted-paramagnetic transitions⁸. In our compounds, since $|k_0| \gg D$, ($\theta = -8.6$ for the Chloride and $\theta = -6.1$ K for the Bromide⁷) we expected also to identify these transitions.

Measurements were made with a.c. Hartshorn bridge (155 Hz) in a cryostat previously described⁹, inserted in a superconducting magnet. The only important modification of the insert cryostat described in ref. 9 was that in the present measurements the pick-up coils were immersed in the same thermal bath as the sample. These were always in powdered form because we have not been able to grow large enough single crystals for accurate measurements.

Fig. 1 shows χ_m (molar susceptibility) versus H at constant T for the $\text{NiBr}_2 \cdot 6\text{NH}_3$ for temperature above and below T_N . Above T_N (at $T = 1.13$ K), χ_m increases slightly up to 50 kOe where it shows a broad maximum. Below T_N ($T = 0.49$ K and $T = 0.34$ K in the figure) four singularities are evident: - close to 10 kOe there is an increase of about 15%; - then χ_m is practically constant up to 37 kOe where a small peak starts a sudden decrease; - this is followed by a rapid increase up to another small peak close to 50 kOe; - above 50 kOe χ_m increases slowly until a λ -peak is reached at 60 - 70 kOe. The temperature dependence of these singularities is seen in fig. 2.

We do not have any reasonable explanation for this striking behavior. Many different (and independently grown)

samples were measured all showing the same results. It is interesting to note that the approximately constant susceptibility above 10 kOe corresponds to the maximum zero-field susceptibility of reference 7 (which occurs near T_N). This suggests that above 10 kOe the spins are perpendicular to the magnetic field since the maximum zero-field susceptibility, at T_N , in the molecular field approximation, corresponds to the perpendicular susceptibility. The increase of $\chi(H)$ at 10 kOe could then correspond to a rotation of the spins to a direction perpendicular to H , a phenomenon similar to the spin-flop transition. In a molecular field approximation, considering only first neighbors interaction and when the exchange energy is much bigger than the anisotropy energy, the transition from the canted phase to the paramagnetic phase at $T = 0$ occurs approximately at

$$H_c(0) \approx -2k\theta/g\beta \quad (1)$$

where k is the Boltzmann constant, g is the spectroscopic factor and β is the Bohr Magneton. The spin-flop field at $T=0$, $H_{SF}(0)$, is given by $H_{SF}(0) = H_c(0) H_A(0)$ where $H_A(0)$ is the anisotropy effective field at $T=0$. Using Yosida's relation between $H_A(0)$ and D^{10} , the uniaxial Spin-Hamiltonian parameter, one gets:

$$\beta^2 H_{SF}^2(0) = -2k\theta D \quad (2)$$

Taking $g = 2.18$ and $\theta = -6.1$ K (from ref. 7) and assuming $H_{SF}(0) \sim 10$ kOe one obtains $H_c(0) \approx 85$ kOe and $D/k \approx 0.2$ K. As it can be seen in fig. 2 this value of $H_c(0)$ is

compatible with an extrapolation to $T = 0$ of the T -dependence of the λ -peak. The value of D can be considered in reasonable agreement with that given by EPR data, and here one should note that precise EPR data was obtained only for the Chloride and that Yosida's relation is exact only for a strictly uniaxial antiferromagnet (it certainly underestimates D when the spins are not all aligned with the anisotropy axes which is quite possible in a cubic material). So, in fig. 2, the extrapolation to $T = 0$ of the lowest and highest points seem to be consistent with what is expected as an $H - T$ phase diagram for the $\text{NiBr}_2 \cdot 6\text{NH}_3$ but we could not find any explanation for the intermediate structure of the susceptibility. Finally we want to point out, here, that the broad maximum observed above T_N may be related to the onset of short range order, which is likely to occur in this sample as the large θ/T_N ratio suggests.

Fig. 3 shows $\chi_m \times H$ at three constant T for the $\text{NiCl}_2 \cdot 6\text{NH}_3$. At 4.14 K χ_m is practically independent of H up to the highest fields measured. At 1.70 K some structure can already be seen. Below 1 K two singularities are evident at relatively low fields and their temperature dependence is seen in fig. 4. At high fields χ_m increases again, but no maximum is reached up to the highest fields measured. Again, we have not been able to explain this field dependence. It is interesting to note, however, that the use of equation (2) with $g = 2.18$, $\theta = -8.6 \text{ K}$ and $D = 0.265 \text{ cm}^{-1}$ yields $H_{SF}(0) \approx 18 \text{ kOe}$ which corresponds perfectly to the extrapolation to $T = 0$ of the lowest points in fig. 4. Equation (1) gives

$H_c(0) \sim 120 \text{ kOe}$ which is far outside our available fields.

The simple model used to derive (1) and (2), although it seems to be consistent with the extrapolation to $T = 0$ of some anomalies found in the low temperature susceptibility, it certainly cannot account for the large θ/T_N ratio. The present data plus the anomalous zero-field temperature dependence of the susceptibility⁷ indicate that the magnetic ordering in these compounds is not just a straight antiferromagnetic ordering as, for instance, it is the case for the isomorphous salt $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{NH}_3$ ⁸.

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FIGURE CAPTIONS

- Fig. 1 - Molar susceptibility versus magnetic field at constant temperatures for the $\text{NiBr}_2 \cdot 6\text{NH}_3$.
- Fig. 2 - Temperature dependence of the singularities of $(\chi \times H) T$ for the $\text{NiBr}_2 \cdot 6\text{NH}_3$ as identified in the text. The arrow indicates T_N as determined from specific heat measurements and the dashed line marks the position of the broad maximum observed above T_N .
- Fig. 3.- Molar susceptibility versus magnetic field at constant temperatures for the $\text{NiCl}_2 \cdot 6\text{NH}_3$.
- Fig. 4 - Temperature dependence of the singularities of $(\chi \times H) T$ for the $\text{NiCl}_2 \cdot 6\text{NH}_3$ as identified in the text. The arrows mark the two peaks observed in the specific heat.

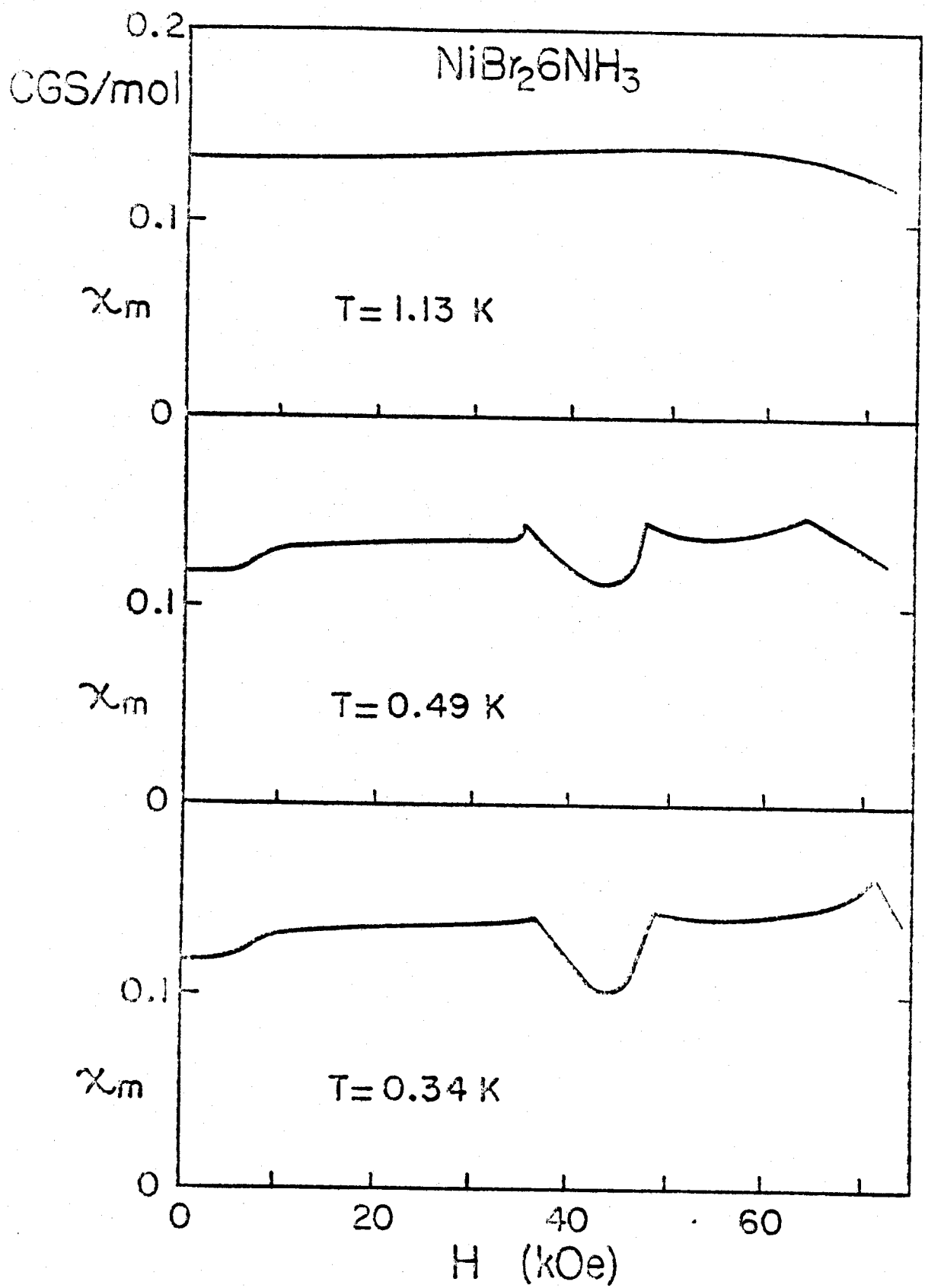


fig. 1

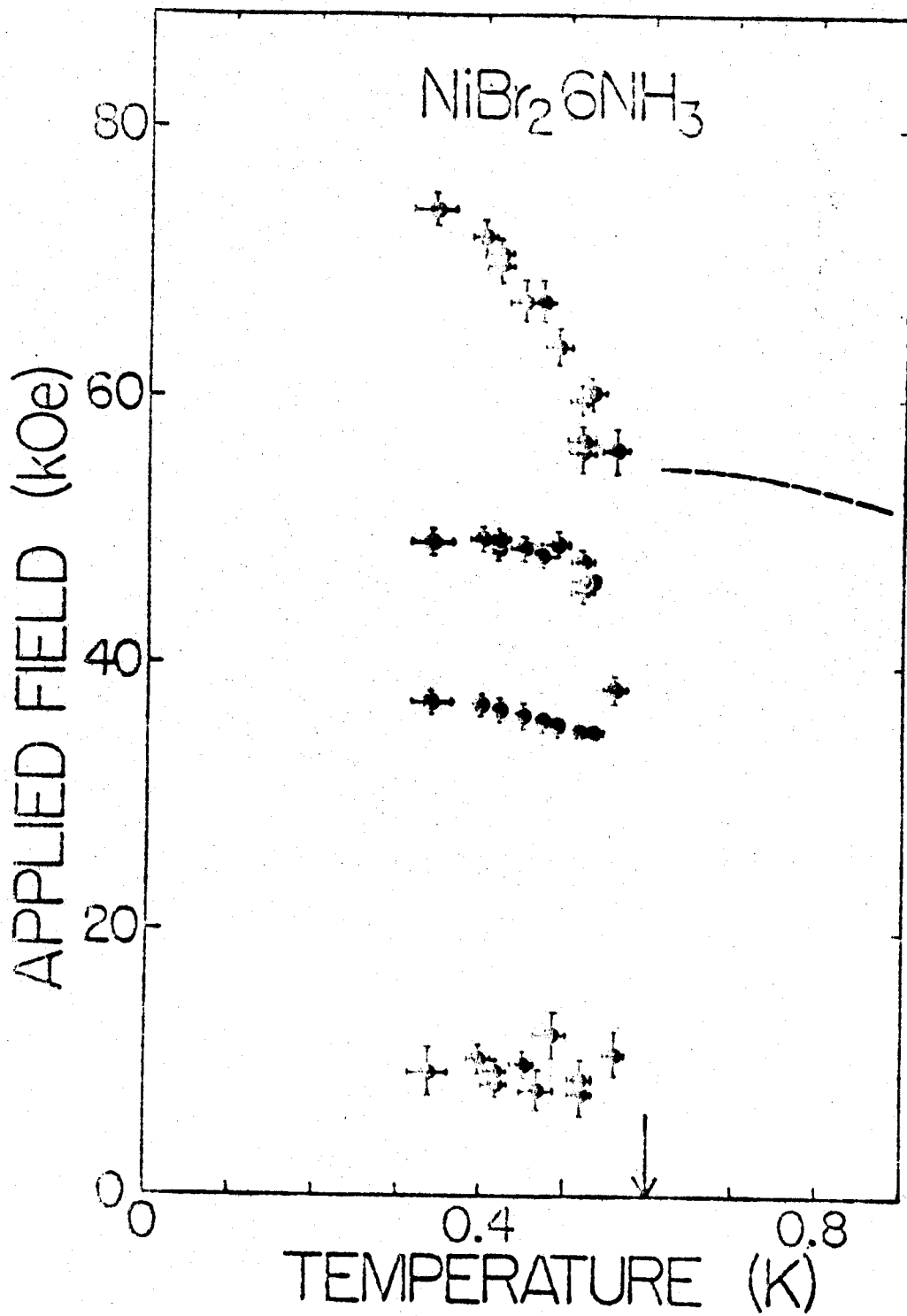


Fig. 2

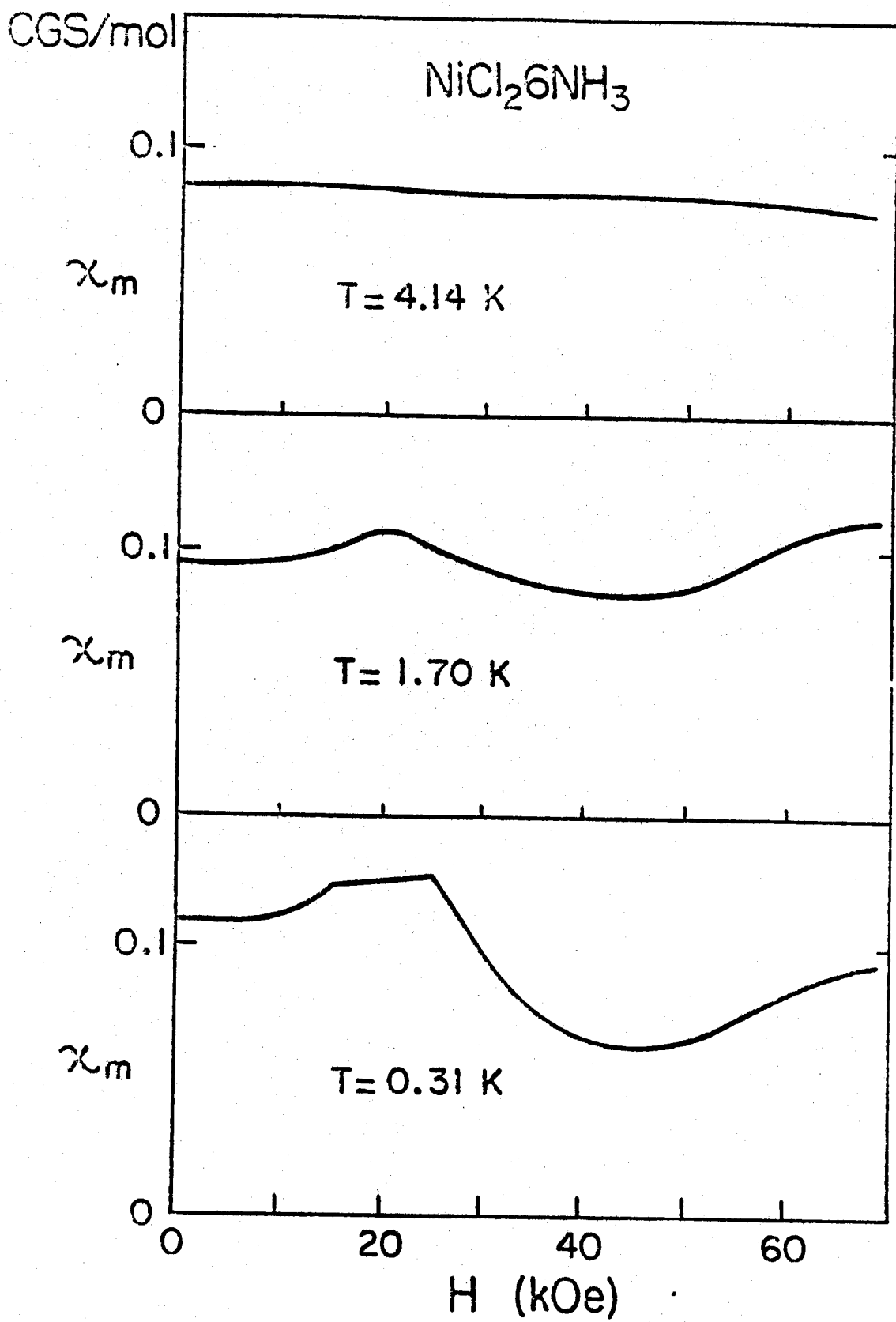


fig. 3

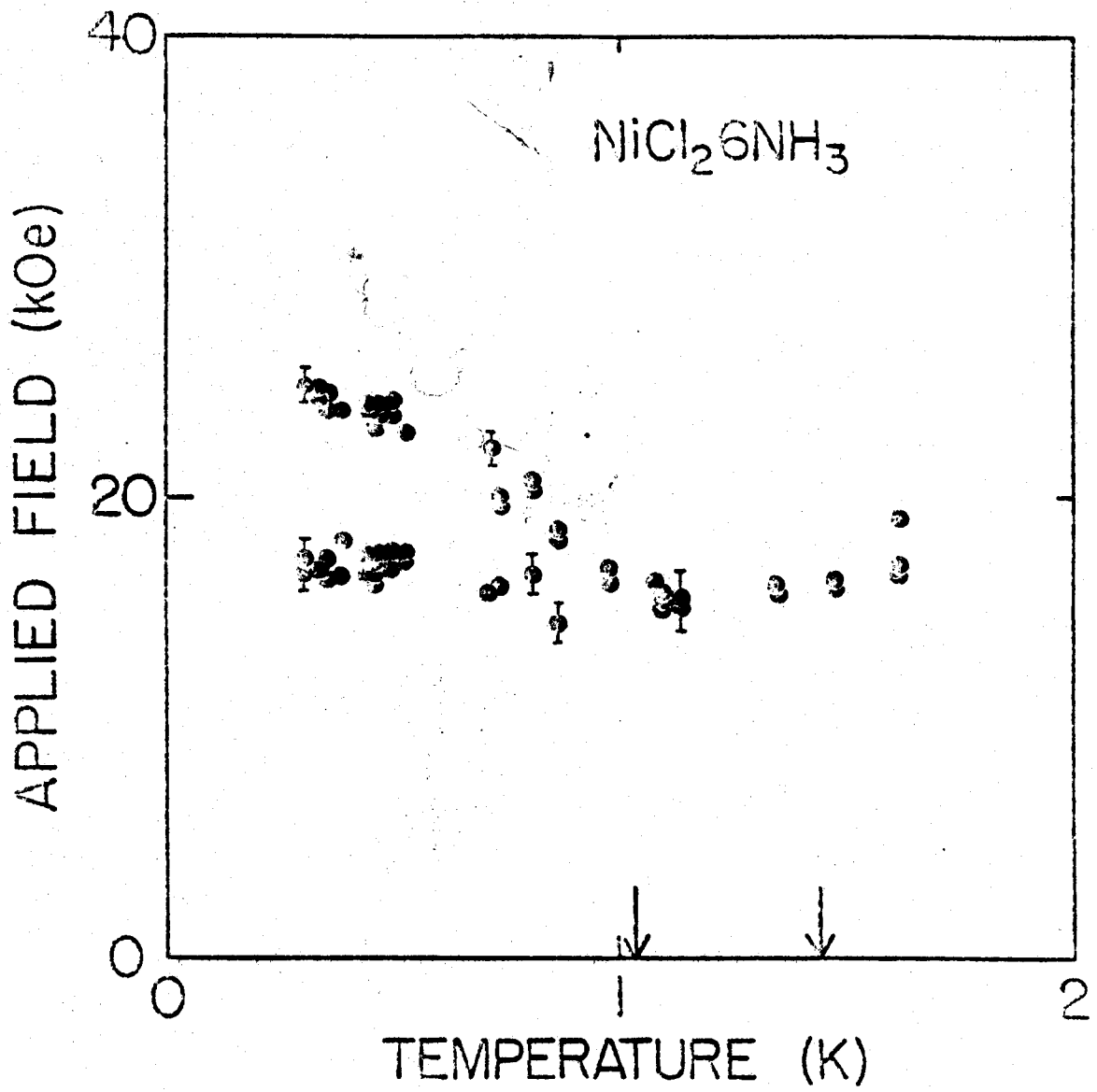


fig 4