

Magnetism at Low Temperature I

Interaction Effects in Potassium Ferricyanide

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The character and magnitude of the exchange interaction between the ferric ions in $K_3Fe(CN)_6$ have been investigated by, (1) observation of the paramagnetic resonance spectrum of coupled Fe-Fe pairs in semi-dilute crystals and, (2) adiabatic demagnetization of concentrated crystals. The results show that the exchange between magnetically similar ions contains an appreciable anisotropic part of the order of 0.07 cm^{-1} . No lines corresponding to dissimilar ion pairs were found. From the two types of experiments, it is concluded that the isotropic part of exchange between similar ions, J_s , is about 0.25 cm^{-1} and that the exchange between dissimilar ions is very small.

The electron configuration of the Fe^{+3} ion in $K_3Fe(CN)_6$ complex is $(d\epsilon)^5$ and the ground state can be described by an effective spin $s=1/2$. Measurements of the Weiss constant by McKim and Wolf¹⁾ have revealed the existence of a large anisotropic exchange. The anomalous large line width of the paramagnetic resonance line has been interpreted as due to this anisotropic exchange²⁾. We have observed paramagnetic resonance in samples diluted by $K_3Co(CN)_6$. Two pairs of lines were observed which could be interpreted as arising from the triplet of an ion pair coupled by anisotropic exchange. The angular dependence of the lines in the bc -plane is shown in Fig. 1. For the more concentrated crystals, the single ion line indicated the coexistence of orthorhombic and monoclinic cells. Fig. 2 shows the principal axes of the ions for the two types of unit cells. It is seen in Fig. 1. that the pairs corresponding to the larger splitting appear to conform with the solid curve calculated by taking the axes of the interaction tensor to coincide with those of the single ion g -tensor for the monoclinic cell. The deviation from the crystal axes is, however, very small ($\sim 2^\circ$ in the bc -plane). In Table 1, the anisotropic exchange calculated from the splittings along the crystal axes are listed. In the present case dipolar interaction amounts to about 20% of the anisotropic part of exchange. This has been

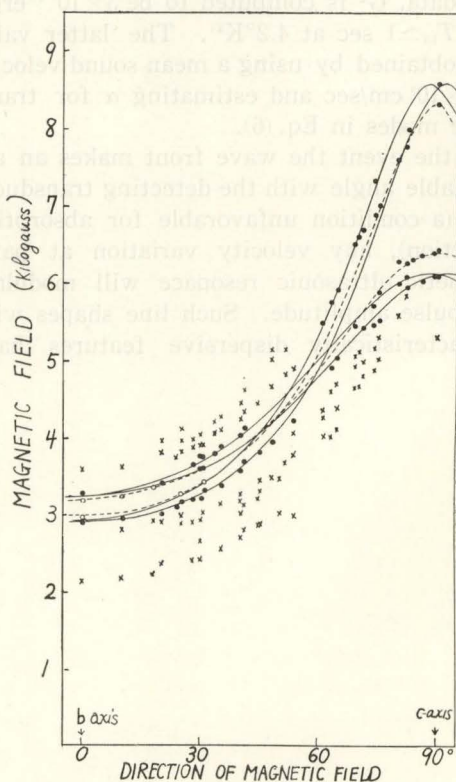


Fig. 1. Angular variation with the field in the bc -plane. The solid line is calculated using J_i of Set II in Table 1. The principal axis is taken to coincide with the g -tensor axis of the monoclinic cell. The dotted line is calculated using J_i of Set I with the axes along the crystal axes.

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Table I.

Set		a	b	c
I	$J_i'^*$	-0.028cm^{-1}	-0.020	$+0.055$
	$d-d^{**}$	$+0.010$	-0.004	0
	J_i^{***}	-0.038	-0.016	$+0.055$
II	J_i'	-0.037	-0.029	$+0.072$
	$d-d$	$+0.010$	-0.004	0
	J_i	-0.047	-0.025	$+0.072$
Average of J_i for I and II		-0.043	-0.021	$+0.064$
J_i' from Weiss const.**** with $n=2$		-0.044	-0.024	$+0.067$

* J_i' denotes the observed splitting.

** Dipolar interaction for similar ion pairs with fields along respective axes.

*** Anisotropic exchange interaction.

**** Due to McKim and Wolf.¹⁾

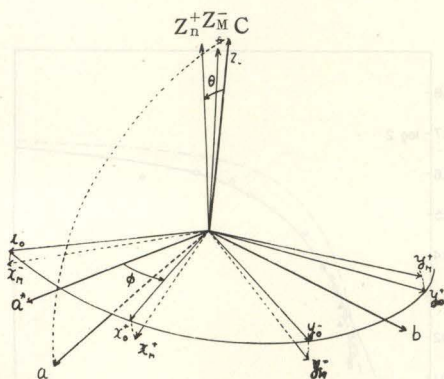


Fig. 2. The principal axes of the g -tensor in semidilute $\text{K}_3(\text{Fe},\text{Co})(\text{CN})_6$. (x_0, y_0, z_0) refer to the orthorhombic cell whereas (x_m, y_m, z_m) refer to the monoclinic cell.

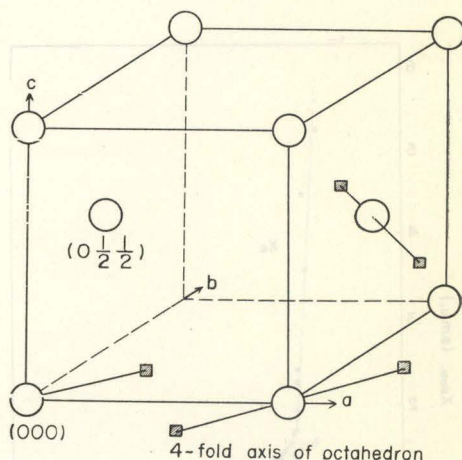


Fig. 3. The unit cell of $\text{K}_3\text{Co}(\text{CN})_6$. 2Co in $(0\ 0\ 0)$; $(0\ \frac{1}{2}\ \frac{1}{2})$, 2K_1 in $(0\ 0\ \frac{1}{2})$; $(0\ \frac{1}{2}\ 0)$, 2K_2 in $\pm(xyz, x, \frac{1}{2}-y, \frac{1}{2}-z)$ with $x=\frac{1}{2}$, $y=\frac{1}{4}$, $z=\frac{1}{8}$. Open circles indicate Co ions. This figure refers to the monoclinic cell with $\beta \sim 107^\circ$, no. of molecules per unit cell $Z=2$. For the orthorhombic cell $Z=4$ but only two nonequivalent Co sites.

corrected for and it has been concluded that both pairs are due to coupled pair of ions in equivalent sites (Fig. 3). It is seen that the average of the two sets is in good agreement with the values derived from the Weiss constants measured by McKim and Wolf if the number of nearest neighbours n is assumed to be two and the dipolar interaction is neglected. This is in accord with the conclusion that the lines are due to similar ion pairs. No lines which could be assigned to pairs of dissimilar ions were observed.

The Weiss constant¹⁾ also gives the sum of the isotropic exchange between similar and dissimilar ion pairs as $J_s + 2J_d = 0.29\text{cm}^{-1}$. Adiabatic demagnetization were made in order

to obtain more information on the isotropic part and to probe into the character of the transition caused by exchange with a known anisotropic part. The results are shown in Figs. 4 to 6. The features to be noted are the large amount of entropy lost (about 85% of the total) before magnetic anomaly is observed and the sharp rise in χ_a near the transition point. The temperature was measured by cerium magnesium nitrate and

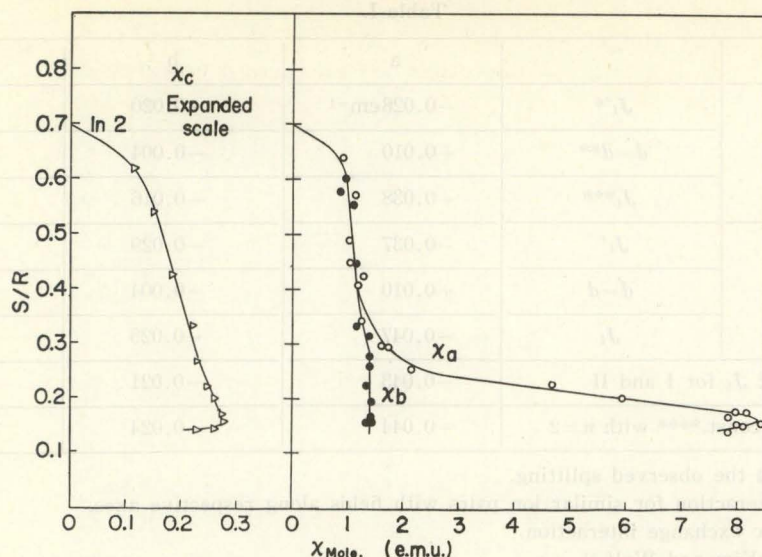


Fig. 4. Entropy versus susceptibility. The scale for χ_c has been expanded.

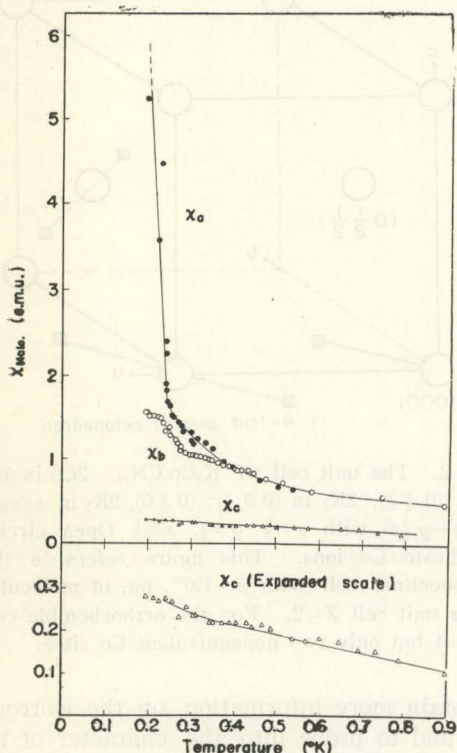


Fig. 5. Susceptibility versus Temperature.

the transition temperature was located at 0.2°K with a probable error of about 20%. The large amount of entropy lost indicates the existence of an appreciable amount of short range order. Such a situation may exist if the exchange between similar ions

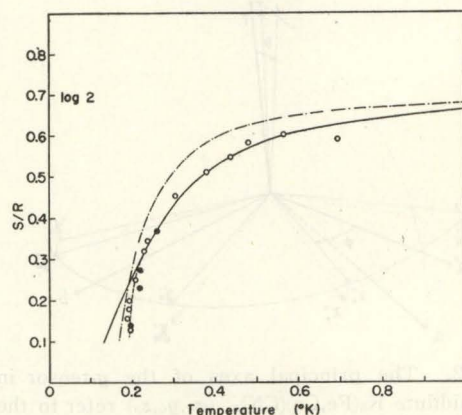


Fig. 6. Entropy versus Temperature.

—○— Sample # 4, —●— Sample # 6.

Solid line: Linear Ising chain with $J_d=0$, $K_c=0.35\text{cm}^{-1}$.

Broken line: Molecular field approximation with $J_d=0$, $J_s=0.29\text{cm}^{-1}$, $J_i=\text{Table 1}$.

is large compared to that of dissimilar ions for then initial ordering will progress within mutually independent linear chains of similar ions. These chains lie along the a -axis. The sign of the total exchange and the values for the anisotropic part indicate that the spins will be aligned antiparallel to each other along the c -axis. The entropy of an Ising chain was calculated using the average J_c and neglecting J_d . The results are shown as a full line in Fig. 6. The deviation near the transition is most probably caused by J_d

which will give rise to long range order. The magnitude of J_d cannot be estimated with certainty but is probably of the order 0.01 cm^{-1} . The sharp rise in χ_a may be interpreted as due to the existence of a small uncompensated magnetic moment along the a -axis in the ordered state. Definite conclusions cannot be made at present but it is probably related to the existence of the monoclinic cell.

References

- 1 F. R. McKim and W. P. Wolf: Proc. Phys. Soc. London **B69** (1956) 1231.
- 2 J. M. Baker, B. Bleaney and K. D. Bowers: Proc. Phys. Soc. London **B69** (1956) 1205.
- 3 For more details refer T. Ohtsuka: J. Phys. Soc. Japan **16** (1961) 1549. The presence of a monoclinic cell was not clear in the earlier results and its presence was not taken into consideration.

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Electron Spin Resonance Linewidths of Face Centred Cubic Ni^{2+} Crystals

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Recent experimental results are reported, which provide a basis for a consistent interpretation of the available data on the electron spin resonance, static susceptibility and specific heat of hexammine nickel halides. These results, although preliminary, show that a well-known motional effect gives rise to a magnetic behaviour of a new type in a class of simple crystals.

As it has been previously reported, face-centred cubic crystals of $\text{NiX}_2 \cdot 6\text{NH}_3$ (where X stays for Cl, Br, I) exhibit a striking magnetic behaviour at low temperatures; the single isotropic electron spin resonance line, which is present at room temperature, undergoes, when the temperature is lowered through a certain critical value, an abrupt and very large broadening which might be, in principle, connected with the appreciable, though not adequately large, exchange effects exhibited by these crystals¹⁾. On the other hand, the mentioned transition is not paralleled by an anomaly in the behaviour of the static magnetic susceptibility vs. temperature¹⁾ and this would suggest²⁾ that motional effects rather than exchange effects could be responsible for the transition. Specific heat experiments performed by Leiden people on the iodide

salt (the specimens for all the different kinds of experiments were obtained in the same preparations) revealed anyway, at the same temperature at which the ESR transition occurs, an entropy anomaly of about $k \ln 3$ times the number of the nickel ions³⁾.

In an attempt to clarify the problem, we have performed⁴⁾ ESR experiments on $\text{NiI}_2 \cdot 6\text{ND}_3$ specimens. These experiments have shown that the substitution of hydrogen by the heavier deuterium, shifts *upwards* the transition temperature (from 19.5°K in $\text{NiI}_2 \cdot 6\text{NH}_3$ to about 26.5°K^* in $\text{NiI}_2 \cdot 6\text{ND}_3$).

This result proves that the transition has

* It has to be noted that the temperatures above 4°K up to about 80°K are here given with an accuracy of a few percents. This is due to a possible inaccuracy in the calibration of the thermometer as well as to possible temperature gradients along the microwave cavity, rather than to the temperature control itself, which works within limits by far much narrower.

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