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Exchange Coupling Between Three Iron Ions in Two Organic Molecules

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FOEX, Tsai, and Wucher[1] have studied the variation of susceptibility with temperature of two organic molecules:

$[Fe_3(CH_3COO)_6(OH)_2]NO_3+6H^2O$ acetate,
$[Fe_3(C_6H_5COO)_6(OH)]\times(C_6H^5COO)(ClO^4)+H^2O$ benzoate,

between the temperatures of 2°K and 293°K. Between 73°K and 293°K the two complexes follow Weiss law with

acetate $\mu_B=5.19$ per atom $\theta=-443°$,
benzoate $\mu_B=5.5$ per atom $\theta=-572°$.

Below 20° they follow another Weiss law:

acetate $\mu_B=1.2$ per molecule $\theta=-2°$,
benzoate $\mu_B=1.26$ per molecule $\theta=-6.°5$.

As suggested by Foex *et al.*, the three spins of the ferric ions must be coupled in such a way as to give a smaller magnetic moment at low temperatures.

The experimental value of χ at high temperatures demand $S=5/2$ for each ion, in accordance with the electronic structure of Fe^{+++}.

The simplest possible interaction between the 3 spins is

$$\mathcal{H}=J(\mathbf{s}_1\cdot\mathbf{s}_2+\mathbf{s}_2\cdot\mathbf{s}_3+\mathbf{s}_3\cdot\mathbf{s}_1)=\tfrac{1}{2}JS(S+1)+\text{const},$$

where S is the total spin. S can take all values between 1/2 and 15/2. Each value, except 15/2, can be obtained in several ways (2 for the ground state $S=\frac{1}{2}$).

The theoretical curve $1/\chi$ against T, obtained with this hypothesis is not unlike the experimental one, except for an important bump which does not actually occur. In order to improve the model, we assume that the interaction between two of the ionic spins $\mathbf{s}_2$ and $\mathbf{s}_3$ is different from the other interactions. The Hamiltonian can be written:

$$\mathcal{H}=J(\mathbf{s}_1\cdot\mathbf{s}_2+\mathbf{s}_1\cdot\mathbf{s}_3)+J(1+\tfrac{1}{2}m)\mathbf{s}_2\cdot\mathbf{s}_3,$$

where m is a parameter

$$\mathcal{H}=\tfrac{1}{2}JS(S+1)+\tfrac{1}{4}mJS'(S'+1),$$

and S' is the resulting spin of $\mathbf{s}_2$ and $\mathbf{s}_3$. The additional interaction $\frac{1}{4}mJS'(S'+1)$ lifts all the degeneracies except those due to orientation. Reduced curves $(1/\chi)/J=f(kT/J)$ can be plotted for different values of m. Some of these curves (particularly $m=0{,}5$) have shapes similar to those of the experimental curves.

To obtain agreement between the experimental and theoretical curves, a value of J/k of the order of magnitude 60, is required. There remains, however, a serious discrepancy at very low temperatures. The existence of a small negative Curie temperature could be explained by assuming a negative intermolecular field.

However, the slope of the low temperature part of the curve, which corresponds to $\mu_B=1.2$ or 1.26, instead of $\mu_B=1$ as demanded by the hypothesis $S=\frac{1}{2}$ for the ground state, is not understood.

It has been thought preferable to wait for more experimental evidence (in particular in replacing of the ferric ions by other ions), before trying a more complicated model.

Note added in proof.—After this work was completed we learned that Dr. Kenjiro Kambe[2] had already proposed this model in 1949 to explain the susceptibility measurements made by Welo[3] in 1928. Welo's measurements did not extend below 200°K, which led Kambe to assume that equal interactions between the three ions gave satisfactory agreement with experiment.

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[1] Foex, Tsai, and Wucher, Compt. rend. **233**, 1432 (1951).

[2] Kenjiro Kambe, J. Phys. Soc. of Japan, **5**, 48 (1950).

[3] L. A. Welo, Phil. Mag. **6**, 481 (1928).

DISCUSSION

C. J. GORTER, *University of Leiden, The Netherlands:* Dr. J. van den Handel has found susceptibility curves for a substance containing organic radicals which are somewhat similar to those mentioned by the preceding speakers (papers of B. Bleaney, and of Yvon, Horowitz, and Abragam).

It seems to be quite frequent that negative exchange interaction does not lead to antiferromagnetism but to saturation within small groups of ions.