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# The Specific Heat of $FeCl_2 \cdot 4H_2O$ Between 1.15° and 20°K*

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The specific heat of $FeCl_2 \cdot 4H_2O$ has been measured between 1.15° and 20°K. At 1.15°K $C_p$ is rising very rapidly with falling temperature suggesting that the antiferromagnetic transition point, whose existence was inferred from previous observations of magnetic susceptibility, has nearly been reached. At higher temperatures $C_p$ exhibits a Schottky anomaly, the rounded maximum occurring at about 3°K. It has been possible to effect a reasonable separation of the lattice specific heat from the measured total and thus to determine the parameters of the Schottky anomaly. These are found to be consistent with the splitting of the spin quintet ground state of the $Fe^{++}$ ion into a lower doublet and upper triplet with a mean separation of 5.7 $cm^{-1}$.

## Introduction

The magnetic susceptibility of powdered $FeCl_2 \cdot 4H_2O$ has recently been observed[1] to pass through a maximum at 1.6°K suggesting the occurrence of an antiferro-paramagnetic transition at a slightly lower temperature. Between 14° and 21°K, the powder susceptibility is well represented by the relation $\chi_m = 3.61/(T+2)$, the Weiss constant, $\theta = 2$°K, being consistent in sign and magnitude with the appearance of antiferromagnetism in the helium region. The observed Curie constant yield a splitting factor $g = 2.19$ if one assumes $S = 2$, i.e, that the orbital angular momentum of the $^5D$ ground state of the free $Fe^{++}(3d^6)$ ion has been quenched by the crystalline electrostatic field and partially restored by spin-orbit interaction.

The crystalline field in this salt is probably of sufficiently low symmetry to remove the orbital degeneracy of the $Fe^{++}$ ground state. One consequence of the spin-orbit interaction should be the splitting of that ground state into five levels corresponding to the removal of the remaining spin degeneracy. The susceptibility data suggest that the overall width of this quintet is $< 10 cm^{-1}$. In the likely event that the zero field splitting should be large in comparison with the interionic (exchange) interaction, the specific heat of $FeCl_2 \cdot 4H_2O$ should exhibit both a cooperative anomaly at the Néel point, $T_N$, and, at a somewhat higher temperature, a Schottky anomaly whose characteristics reflect general features of the level scheme. The behavior of this salt should thus be in interesting contrast with that of $NiCl_2 \cdot 6H_2O$ in which the zero field splitting of the $Ni^{++}$ ground triplet and the exchange interaction are probably of comparable magnitude. In the latter substance a single specific heat anomaly has been observed,[2] that being of a cooperative nature.

## Experimental Results and Discussisn

The heat capacity of 0.202 moles of $FeCl_2 \cdot 4H_2O$ (Fisher's Reagent Grade) in the form of small crystals of average dimension ~2mm contained in a copper capsule has been measured between 1.1° and 20°K in a vacuum calorimeter as described elsewhere.[2] Supplementary data have also been taken on a large single crystal (0.0497 moles) with attached heater and resistance thermometer in order to avoid the difficult correction required in the capsule technique for condensing exchange gas near 1°K. Representative values of $C_P$ from several independent experimental runs are displayed graphically in Fig. 1. The spread of all data taken is accurately indicated by these values.

Evidence for the occurrence of both of the expected anomalies is found in the temperature variation of $C_P$. At 1.15°K, $C_P$ is observed still to be rising quite rapidly with falling temperature in the manner characteristic of a cooperative system immediately above its transition temperature. In this case the transition is presumably an antiferro-paramagnetic one whose Néel point,

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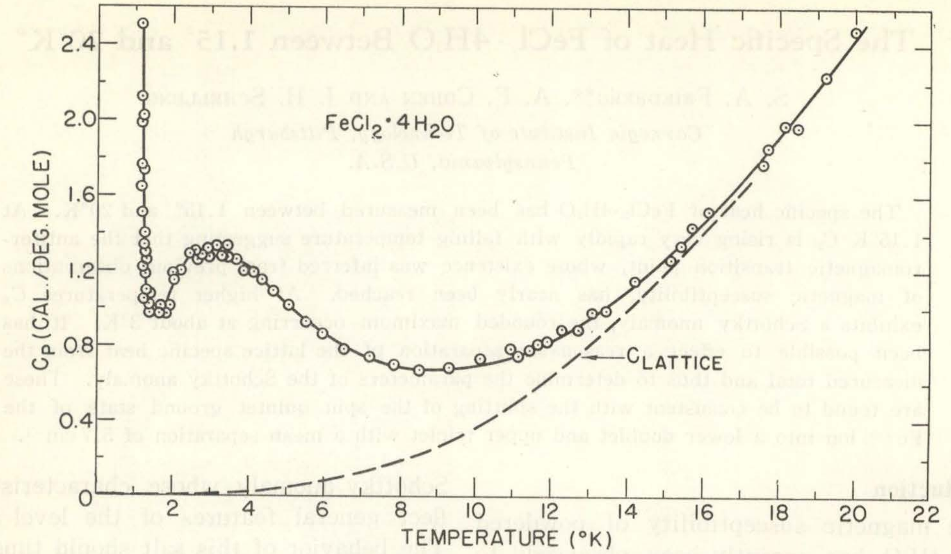

Fig. 1. The molar specific heat of $FeCl_2 \cdot 4H_2O$ between 1.1° and 20°K.

$T_N$, probably occurs very near 1.1°K. Unfortunately it has not been possible to reach $T_N$ in the present series of measurements.* This work, however, is continuing in an effort to extend the results to the region below 1°K.

The anticipated Schottky anomaly is clearly resolved, the rounded maximum occurring at $T_{\max} \sim 3$°K. At sufficiently high temperatures this anomaly should go to zero as $T^{-2}$. If in this region the lattice contribution to $C_P$ is still varying as $T^3$, we may expect a plot of $C_P T^2$ vs $T^5$ to yield a straight line. The data obtained above 3°K are plotted in this way in Fig. 2. Between about 7° and 15° a linear region is rather clearly defined. In this interval the measured specific heat obeys the relation $C_P/R = 1.78 \times 10^{-4} T^3 + 16.5 T^{-2}$. The lattice term is comparable with those found for similar hydrated salts.[2)] Ignoring possible temperature variation of $\theta_D$, an approximate correction for the lattice specific heat, $C_{\text{lattice}}$ may be computed. This correction is shown as a dashed curve in Fig. 1 and will be seen to be quite small at 3°K where the Schottky anomaly has its maximum value $C_{\max} \sim .64R$.

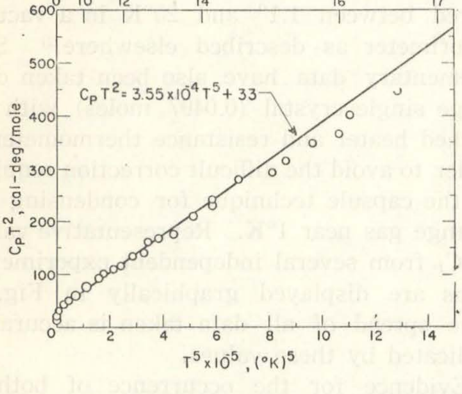

Fig. 2. $C_P T^2$ as a function of $T^5$ for $FeCl_2 \cdot 4H_2O$.

The height of a Schottky anomaly is quite sensitive to the grouping of the levels which produce it. In particular, should we have five levels grouped into an upper degenerate triplet and a lower degenerate doublet it is easy to show that $C_{\max} = .62R$, very nearly the observed value. While the number of levels and their distribution are not uniquely determined by the value of $C_{\max}$, certain other arrangements of five levels are excluded such as, for example, a lower triplet and upper doublet ($C_{\max} = .28R$). It is noteworthy that if it is assumed that the $Fe^{++}$ ground state has five components grouped into a lower doublet and an upper triplet then two other obser-

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* In the preliminary version of this report it was stated that $C_P$ actually passed through a maximum value at 1.26°K which was identified as $T_N$. Recent single crystal data indicate, however, that this maximum was spurious, probably the result of incomplete correction of the data obtained by the capsule technique for condensing helium exchange gas.

vations on the Schottky anomaly are rended consistent. A doublet-triplet separation $\delta$ may then be deduced either from the temperature $T_{\max}$ of the anomalous maximum or from the coefficient $A$ of the high temperature limiting expression for the magnetic specific heat $A/T^2$. The relevent formulae are easily derived, namely, $\delta=2.54T_{\max}$ and $\delta=(25A/6R)^{\frac{1}{2}}$. Using $T_{\max}\sim 3$°K and $A/R=16.5(°\mathrm{K})^2$ as indicated above, one finds $\delta$ values of 7.6°K ($=5.4\,\mathrm{cm}^{-1}$) and 8.3°K ($=5.9\,\mathrm{cm}^{-1}$). The agreement between these values is rather satisfactory and suggests that the simplified partition function $z=2+3e^{-\delta/T}$ provides an adequate description of the Schottky anomaly at least in and above the region of the maximum. It is unlikely, of course, that the components of either the doublet or the triplet are completely degenerate as assumed. It would appear, however, that these splittings are substantially smaller than $\delta$. From the location of the cooperative anomaly it is evident that the doublet splitting is no more than $\sim .8\,\mathrm{cm}^{-1}$ and that during this transition the $Fe^{++}$ ion might be regarded as possessing an effective spin of $\frac{1}{2}$.

Tinkham[4] has calculated the splitting of the ground quintet of $Fe^{++}$ in a crystalline field of rhombic symmetry using the spin Hamiltonian $D_{ij}S_iS_j$. Although exchange effects were not included, the results are suggestive of the general scheme expected for $Fe^{++}$ in the distorted inhomogeneous octahedral environment[3] provided by $FeCl_2 \cdot 4H_2O$. For reasonable relative magnitudes of the principal components of $D_{ij}$, i.e., $D_x$, $D_y$, $D_z$, one finds the quintet divided into a closely spaced doublet and a more open triplet. Whether it is the doublet or triplet which lies lowest depends upon the sign of $D_z$, and for $Fe^{++}$ as an impurity in $ZnF_2$ the doublet was found[4] to be lowest. Qualitatively Tinkham's model appears capable of reproducing the features of the $Fe^{++}$ ground state in $FeCl_2 \cdot 4H_2O$ inferred from the Schottky anomaly in the low temperature specific heat. An analysis including exchange effects along the lines indicated by Moriya et al[5] should probably be attempted only after single crystal susceptibility and paramagnetic resonance studies of this salt now in progress are completed.

It is interesting to note that specific heat measurements on the Tutton salt $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ by Hill and Smith[6] reveal no cooperative effects. Instead, two Schottky anomalies are found which can be interpreted as arising from a quintet $Fe^{++}$ ground state divided into a lower doublet split by $6.5\,\mathrm{cm}^{-1}$ and a triplet about $38\,\mathrm{cm}^{-1}$ above the lowest level. The corresponding intervals inferred from the present results are $<.8\,\mathrm{cm}^{-1}$ and $5.7\,\mathrm{cm}^{-1}$. This relative reduction in the ground state splitting probably reflects differences in the electrostatic environment of $Fe^{++}$ in the two salts. In the Tutton salt this environment is provided by a slightly distorted octahedron of six $H_2O$'s at distances of about 2.1Å. In the chloride the octahedron[3] is composed of four $H_2O$'s (two at 2.09Å and two at 2.59Å) and two $Cl^{-1}$'s at 2.38Å. The departure of the crystalline field from cubic symmetry is much greater in the chloride. We may expect therefore, the first excited state of $Fe^{++}$ arising from the orbital triplet left by a cubic field to be separated from the ground state by an energy $\Delta E$ which is larger in the chloride than in the Tutton salt. The width of the spin quintet comprising the ground state is of the order of $\frac{\lambda^2}{\Delta E}$ where $\lambda$ is the spin-orbit constant. The reduced width in the chloride thus is attributable to the higher asymmetry of its crystalline field.

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