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Nuclear Specific Heats in Paramagnetic Salts*

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This paper considers theoretically the contribution to the specific heat arising from the hyperfine structure, i.e., from the interaction of the magnetic moment and electric quadrupole moment of the nucleus with its surroundings. This contribution is important only at low temperatures, where it is approximately of the form A/T^2. The coefficient A is calculated for a number of copper, manganese, and cobalt salts. Agreement with the limited amount of experimental data available is reasonably good. The influence of the hyperfine structure on the magnetic susceptibility is negligible unless the temperature is exceedingly low, for even in single crystals it begins only with terms of the third order in a series development in $1/T$. In manganese ammonium sulphate, the electronic Stark splitting deduced from paramagnetic resonance at 20° and 90°K does not agree with that obtained from the paramagnetic anisotropy between 90° and 300°K.

IN paramagnetic salts where the nucleus of the paramagnetic ion possesses a spin, a hyperfine structure is observed in the paramagnetic resonance spectrum caused by interaction between the nucleus and the electron shell of the ion. This interaction consists of two parts; a magnetic interaction between the nuclear magnetic moment and the magnetic field due to the spin and the unquenched residual orbital momentum of the electron, and an electric interaction between the nuclear quadrupole moment and the gradient of the electric field produced by the electronic charge. Exact evaluation of these effects is difficult owing to the enormous crystalline electric field, but when the latter has axial symmetry it has been found that the Hamiltonian

$$AS_zI_z+B(S_xI_x+S_yI_y)+Q\{I_z{}^2-\tfrac{1}{3}I(1+1)\} \qquad (1)$$

accounts for the observed hyperfine structure. (Here S and I refer to the electronic and nuclear spins, respectively.) The constants A, B, and Q can then be determined directly by microwave measurements.

The nuclear interaction gives rise to a hyperfine structure of the energy levels which affects the thermal properties of the salt at very low temperatures. An anomalous specific heat maximum should be observed below 1°K, the tail of which can be detected, for example, by paramagnetic relaxation measurements in the helium region (Benzie and Cooke[1]). This tail can be evaluated as a power series in $(1/T)$, of which the first term is

$$C/R=(1/T^2N^2)\{N\textstyle\sum_iW_i{}^2-(\sum_iW_i)^2\}(hc/k)^2,$$

where the W_i are the energy levels (in cm^{-1}) in zero magnetic field, and N is the total number of such levels $=(2S+1)(2I+1)$. The two terms $\sum_iW_i$ and $\sum_iW_i{}^2$ are simply the traces of the matrices for the energy and the square of the energy, and their evaluation yields the result

$$(CT^2/R)=(hc/k)^2\{(1/9)(A^2+2B^2)S(S+1)I(I+1) \\ +(1/45)Q^2I(I+1)(2I-1)(2I+3)\}, \qquad (2)$$

where A, B, and Q are in cm^{-1}.

This result may be applied to a number of salts where the constants A, B, and Q have been determined.

For the copper Tutton salts, measurements of Ingram[2] give

	A	B	Q	CT^2/R (calc.)
Copper ammonium sulphate	0.0133	0.0020	0.0009	1.2×10^{-4}
Copper rubidium sulphate	0.0119	0.0009	0.0011	1.0×10^{-4}.

The values of CT^2/R are in good agreement with the direct measurements of Benzie and Cooke,[1] which give 1.1×10^{-4}.

In cobalt salts, paramagnetic measurements by Bleaney and Ingram[3] and their interpretation by Pryce[4] show that the ground electronic state is a Kramers' doublet, which may be treated as a case of $S=\frac{1}{2}$. The value of I is 7/2. Two salts have been examined:

	A	B	CT^2/R (calc.)
Cobalt ammonium sulphate	0.024	0.0028	16×10^{-4}
Cobalt fluosilicate	0.020	0.0052	12×10^{-4}.

The magnitude of Q has not yet been determined, but appears to be small. Preliminary measurements of Benzie and Cooke give $CT^2/R=17\times10^{-4}$ for the cobalt ammonium sulphate.

In the case of manganese, the nuclear spin is 5/2, and the electronic spin is also 5/2. The electronic levels are split, and in the first approximation can be fitted by an additional term, suggested by Pryce,

$$D\{S_z{}^2-\tfrac{1}{3}S(S+1)\} \qquad (3)$$

in the Hamiltonian. This will give a contribution to the specific heat similar to that due to the term in Q.

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[1] R. J. Benzie and A. H. Cooke, Nature 164, 837 (1949).

[2] D. J. E. Ingram, Proc. Phys. Soc. London 62A, 664 (1949).

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Preliminary analysis of two salts gives the values

	A	B	D	CT^2/R (calc.)
Manganese ammonium sulphate	0.009	0.009	-0.028	1.4×10^{-2}
Manganese fluosilicate	0.009	0.009	$+0.014$	0.7×10^{-2}.

The sign of D is determined from second-order effects in the paramagnetic resonance spectrum.

In manganese ammonium sulphate there appears to be a small departure from tetragonal symmetry, which would give an additional specific heat increasing the total by about 5 percent. This would bring it into agreement with preliminary measurements of Benzie and Cooke. No quadrupole term has been detected, and its contribution to the specific heat is probably negligible.

In general the signs of A, B, and Q have not yet been determined, but this does not affect the values of CT^2/R since only the squares are involved. Interpretation of adiabatic demagnetization measurements on these salts requires a knowledge of the energy level system in zero magnetic field, which cannot be given exactly without determination of these signs. Nevertheless it may be of interest to give the levels for copper ammonium sulphate, assuming A positive, for the alternative cases of Q having positive and negative signs. These levels are independent of the sign of B, but should be inverted on reversing all the signs.

	$Q=+0.0009$ cm^{-1}	$Q=-0.0009$ cm^{-1}
Doublet	0.0109 cm^{-1}	0.0091 cm^{-1}
Doublet	0.0027	0.0044
Singlet	-0.0022	-0.0004
Singlet	-0.0062	-0.0044
Doublet	-0.0093	-0.0110.

The over-all separation is 0.020 cm^{-1} in each case, and it seems that curves of entropy etc. will be almost independent of the signs of A, B, and Q until temperatures of the order of 0.01°K are reached.

For cobalt the level system consists of seven doublets and two singlets; for cobalt ammonium sulphate the relatively small value of B means that these may be approximately taken as eight equally spaced doublets with an over-all splitting of 0.084 cm^{-1}.

For manganese the system will contain 15 doublets and six singlets, the over-all splitting being about 0.3 cm^{-1} and 0.2 cm^{-1} for the ammonium sulphate and fluosilicate respectively.

SUSCEPTIBILITY

The diagonal sum method may be applied to the calculation of the susceptibility as a power series in $1/T$. It turns out that the hyperfine structure leaves the term in $1/T$ unaltered, and introduces no term in $(1/T)^2$ even for a single crystal. Thus the hyperfine structure cannot be detected by the presence of an effective "Weiss constant" in the susceptibility.

This behavior contrasts with that due to an electronic splitting, which gives rise to terms in $(1/T)^2$ in the principal susceptibilities. With the Hamiltonian (3) above one finds

$$\begin{aligned}\chi_{\parallel}&=\frac{Ng_{\parallel}{}^2\beta^2S(S+1)}{3kT}\left\{1-\frac{D(2S-1)(2S+3)}{15kT}\right\}\\ \chi_{\perp}&=\frac{Ng_{\perp}{}^2\beta^2S(S+1)}{3kT}\left\{1+\frac{D(2S-1)(2S+3)}{30kT}\right\}.\end{aligned}\tag{4}$$

The second-order terms average to zero for a powder, as pointed out by Van Vleck and Penney.[5]

These formulas may be used to obtain an independent estimate of D for manganese. The best measurements of anisotropy in manganese ammonium sulphate are those of Krishnan, Mookherji, and Bose[6] between room temperature and 90°K. With two ions in unit cell, two interpretations are possible, giving $D=-0.057$ cm^{-1} or $+0.059$ cm^{-1}. These are clearly too large, as the specific heat due to the electronic splitting alone would then be greater than that observed in the undiluted salt.[7,8] Moreover the paramagnetic measurements resolve the ambiguity of interpretation, and show that the measured anisotropy corresponds to $D=+0.059$ cm^{-1}, i.e., that the sign is wrong. As however the maximum anisotropy observed was about 1 in 400, the discrepancy is not surprising.

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