Magnetic Studies of Cerium Ammonium Sulphate in Relation to Crystal Structure

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The magnetic anisotropy and principal magnetic susceptibility of the single crystal of cerium ammonium sulphate has been measured and the results obtained have been discussed in the light of crystalline field theory. It has been observed that the cubic field in cerium ammonium sulphate is very much stronger and the contribution of the rhombic field is almost negligible. The predominance of the cubic field over the rhombic field may also be due to surrounding of the cerium ion by octahedron of water molecules with their negatively charged oxygen atoms pointing towards the central Ce$^{3+}$ ion. The relative orientation of the atomic groups with different ions in the unit cell makes the resultant anisotropy smaller.

1. Introduction

The entropy of paramagnetic solids may be regarded as partly thermal and partly associated with magnetic properties. The reason of associating entropy of these solids with their magnetic properties mainly lies in the fact that it refers to a measure of the randomness of distribution. In view of these facts, Debye and Giauque envisaged the possibility of producing the temperatures below 1 K by adiabatic demagnetisation. Giauque and Clark deduced the conditions for producing such temperatures. The production of low temperatures such as below 1 K is of very great significance because the electrical properties at these temperatures begin to behave abnormally. Rare earth salts have been found quite satisfactory for achieving the desired purpose. As such, the study of magnetic properties of rare earth salts has formed of very interesting subject and has engaged the attention of quite a large number of workers. Moreover, in rare earth ion $M^{3+}$, all the inner shells except 4f and the outer 5s and 5p shells are fully occupied but the 4f shell is filled progressively according to the serial order of the rare earth ion. The electrons of the incomplete 4f shell responsible for the paramagnetic behaviour of the ion would partly be shielded by 5s and 5p electron shells from the strong electric fields in these rare earth crystals and this shielding action of the outer shells will greatly reduce the influence of the crystalline field in the crystal which would ultimately affect the paramagnetism of the rare earth ion. Under these circumstances, the quantum number $J$ representing the total angular momentum cannot be taken as a good quantum number and thus the rare earth ions would retain characteristics of their free states. The principal axes associated with various ions in the unit will be oriented relatively to one another in order to form the symmetry of the unit cell from the individual paramagnetic units already present. Therefore, the observed magnetic anisotropy of the single crystal will represent the average effect of the different ions in the unit cell which have been oriented relatively to one another rather than the anisotropy of the individual ions in the unit cell. In this way, the symmetry of the crystalline field is expected to deviate reasonably whenever there are two or more ions in the unit cell. Hence the problem of explaining the observed magnetic properties of the crystal in terms of the crystal structure, magnitude and asymmetry of the crystalline field would become sufficiently complicated.

In this paper, the results of the magnetic properties of the single crystal of cerium ion have been discussed in the light of crystalline field theory developed by Bethe, van Vleck, Penney and Schlapp.

2. Experimental

Crystals were grown out of the aqueous solution of very high purity specimen of cerium ammonium sulphate. The crystals obtained were tested by X-ray
methods and only the single crystals were chosen for magnetic measurements.

The magnetic measurements at room temperature involved three of the followings:
1. The determination of the direction of the principal magnetic axes.
2. The measurement of the difference between the principal susceptibilities.
3. The determination of the absolute susceptibility along any one convenient direction in the crystal.

The experimental methods used for the above measurements were the same as described in the previous paper of the author and the measurement of absolute susceptibility along any one convenient direction in the crystal was carried out by an electrodynammic microbalance developed by Neogy and Lal.

3. Results

The crystals were monoclinic prisms. Here \( \chi_2 \) represents the gram-molecular susceptibility along the \( \mathbf{b} \) axis while the greater of the two in the \((010)\) plane is \( \chi_1 \) and the smaller \( \chi_2 \). \( \psi \) is the angle which the crystallographic \( \mathbf{c} \) axis makes with the \( \mathbf{x}_1 \) axis.

The effective magnetic moment of the crystal is calculated by:

\[
\mu_I = 2.84 \left( \chi_1 - \chi_2 \right) \cdot T^{-1} \cdot \text{a}
\]

where \( \chi_1' \) represents the susceptibilities corrected for diamagnetism for both cation and anion. Diamagnetic corrections for the different groups were taken as given below according to Selwood:

\[
\text{Table I. Magnetic anisotropy at 27 °C.}
\]

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Crystallographic data</th>
<th>Mode of suspension</th>
<th>Orientation in magnetic field</th>
<th>( \Delta \chi )</th>
<th>Magnetic anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NH₄)₂(SO₄)₂ · 4H₂O</td>
<td>Monoclinic</td>
<td>( \mathbf{b} ) axis vertical</td>
<td>( \psi = 78.1^\circ )</td>
<td>188</td>
<td>( \chi_1 - \chi_2 = 188 )</td>
</tr>
<tr>
<td>Ce(NH₄)₂(SO₄)₂ · 4H₂O</td>
<td>( a:b:c = 0.360:1:2.004 )</td>
<td>( \mathbf{c} ) axis vertical (100) plane horizontal</td>
<td>( \mathbf{b} ) axis normal to field</td>
<td>106</td>
<td>( \chi_1 - \chi_2 = 133 )</td>
</tr>
<tr>
<td>Ce(NH₄)₂(SO₄)₂ · 4H₂O</td>
<td>( \beta = 97^\circ 15' )</td>
<td></td>
<td></td>
<td>68</td>
<td>calcd ( \psi = 78^\circ 5' )</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Direction along which susceptibility was measured</th>
<th>Density of the crystal</th>
<th>Volume susceptibility</th>
<th>Corresponding g.mole susceptibility 10⁻⁴ [c.g.s./mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(NH₄)₂(SO₄)₂ · 4H₂O</td>
<td>( x_1 ) -axis</td>
<td>2.523</td>
<td>12.1</td>
<td>2025</td>
</tr>
</tbody>
</table>

\( \chi_1 = 2025 \cdot 10^{-6} \text{ [c.g.s./mole]}; \chi_2 = 1837 \cdot 10^{-6} \text{ [c.g.s./mole]}; \chi_3 = 1892 \cdot 10^{-4} \text{ [c.g.s./mole]} \)
into doublet level above and a quartet below. When the rhombic field is superimposed over the cubic field, the quartet splits into the doublet (Fig. 1).

This two-fold degeneracy retained by each of the three levels is of the spin type. As the Ce³⁺ ion has an odd number of electrons so even in strong field the separation of these doublets will be very small i.e., 0, 153, 696 cm⁻¹ respectively as calculated by Kramers' formulation. The observed value of the mean magnetic moment also agrees with the calculated value.

4.1 Magnetic anisotropy in relation to crystal structure

Taking a similarity in the structure with the crystal of cerium ethyl sulphate, it may be safe to assume that the monoclinic cell of the substance under study contains two molecules in the unit cell. In this case, the principal susceptibilities of one of the molecules can be obtained from those of the other by reflection in the (010) plane of the crystal. We assume the approximate axis of magnetic symmetry along the normal to the plane containing the Ce³⁺ion and parallel to the plane containing the oxygen atoms. Let the gram-molecular susceptibility be represented by $K_{\|}$ and that along the direction in the plane just referred by $K_{\perp}$. Now in view of the uni-axial symmetry possessed by the paramagnetic unit, the $x_2$-axis should evidently be the direction along which both the above mentioned planes intersect and the $x_1$-axis should be the projection of the normals to the planes just mentioned on (010) plane. Let these normals make an angle $\phi$ and $\phi$ respectively with the (010) plane. Evidently we get:

$$x_2 = K_{\perp}; \quad x_1 = K_{\parallel} \cos^2 \phi + K_{\perp} \sin^2 \phi; \quad x_3 = K_{\parallel} \sin^2 \phi + K_{\perp} \cos^2 \phi.$$

From the above equations we get:

$$K_{\parallel} - K_{\perp} = (x_1 - x_2) + (x_3 - x_2)$$

$$= \frac{x_1 + x_2 + x_3}{3}$$

$$= x = \frac{K_{\|} + 2K_{\perp}}{3} = \overline{K}.$$

Substitution of the values of $x_1, x_2, x_3$ gives:

$$K_{\parallel} - K_{\perp} = 243 \times 10^{-4} = \Delta K \text{ and } \overline{x} = 1918 \times 10^{-8} = \overline{K}.$$

The anisotropy $\Delta K/\overline{K} = 243/1918 = 12.6\%$.

5. Conclusion

From the above discussions it may be concluded:

a. The cubic field in cerium ammonium sulphate is very much stronger. This may also be due to this fact that the cerium ions are perhaps surrounded by an octahedron of water molecules with their negatively charged oxygen atoms pointing towards the central Ce³⁺ ion.

b. The relative orientation of atomic groups with different ions in the unit cell averages out the anisotropies of the groups and makes the resultant anisotropy much smaller i.e. 12.6%.