

increased electronic mobility in titanium dioxide². A similar phenomenon has been observed with dry quartz sand². The electronic conductivity of rutile titanium dioxide below 300° C. is at a maximum along the *c* axis of the crystal²; this is consistent with the orientation of the particles in Fig. 5. On the evidence available at present, we prefer this mechanism to that described in section (a).

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¹ Verwey and Overbeek, "Theory of Stability of Lyophobic Colloids" (Amsterdam, 1948).

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Temperature Variation of the Principal Magnetic Moments of Co⁺⁺ Ions and the Asymmetry of the Crystalline Electric Field in Cobalt Acetate Tetrahydrate

THE ground-state of the free divalent cobalt ion is $3d^7$, $^4F_{9/2}$, and the potential due to the crystalline electric field in the neighbourhood of the six co-ordinated cobalt ion conforms to:

$$V = D(x^4 + y^4 + z^4) + Ax^2 + By^2 - (A + B)z^2$$

the fourth-order terms in the expression represent the cubic, and the quadratic terms the rhombic, part of the field. The observed magnetic properties can then be explained on the assumption that the field is predominantly cubic in symmetry with a feeble rhombic component superposed. If the field is due to an octahedral distribution of water molecules around the Co⁺⁺ ion, the seven-fold orbital degeneracy is split into two triplets and a singlet, and the sign of the cubic field coefficient is such as to make one of the triplets the ground-state, the separation of which from the other triplet is of the order of 10^4 cm.⁻¹. With such a disposition of the orbital Stark pattern, the components of the lower triplet being further separated to the extent comparable to kT by the rhombic part of the field, and the spin-degeneracy slightly raised through the spin-orbit coupling, the calculations of the principal magnetic moments naturally become very complicated. Schlapp and Penney¹ have, however, made detailed theoretical calculations of the principal magnetic moments of cobalt salts. Assuming the cubic field to be always of the same intensity, and one of the rhombic field constants zero, they assign different values to the other, namely, $A = 0, 40, 200$, etc. With a small rhombic field the effective magnetic moments naturally become different, but they decrease in more or less the same way as with a purely cubic field when the temperature is lowered. The principal moments separate out further when A is 200, and with the fall of temperature the moment having the largest value increases, reaches a maximum and then falls, while the other moments decrease. From the experimental magnetic data on cobalt salts² it seems that the rhombic field in them is not so strong as to produce a rise in the maximum magnetic moment referred to above.

In the Tutton salts the field is determined almost wholly by the octahedron of water molecules imme-

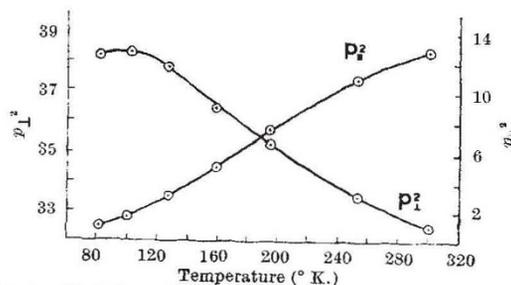


Fig. 1. Variation of magnetic moments with temperature for cobalt acetate

diately surrounding the ion, and hence the deviation from the cubic symmetry will be small. If, on the other hand, the members of co-ordination of the cobalt ion be not all alike, then there will be a possibility of the rhombic field becoming stronger. It seems that cobalt acetate tetrahydrate is a case in point as revealed from its fine structure studies by X-rays³. The space group is $P2_1/c$, and the unit cell contains two molecules. Each cobalt ion is surrounded octahedrally by four water molecules and two oxygens of acetate groups. The cobalt-water (2.11 and 2.06 Å.) and the cobalt-oxygen (2.12 Å.) distances suggest that as in nickel salts the moment in the plane containing the Co⁺⁺ ion and the oxygens of water molecules and of acetate groups is greater than in the direction normal to it.

The room temperature measurements⁴ show that the magnetic anisotropy of cobalt acetate is highest of all the cobalt salts studied so far, and it clearly indicates a strong non-cubic field. We have, therefore, measured the temperature variation of the principal magnetic susceptibilities of the crystal down to liquid air temperature. The results are shown graphically in Fig. 1. The trend of the magnetic moment versus temperature curves supports the existence of a strong rhombic field around the Co⁺⁺ ion in $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

The work will be reported upon more fully elsewhere.

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Visible Absorption Spectra of Copper-ethylene-diamine-bis(acetylacetonate) in the Crystalline State

FOR square planar copper complexes the crystal field theory predicts a splitting of the five-fold degenerate *d*-orbital energy-levels into four energetically different levels, d_{xy} , d_{z^2} , $d_{x^2-y^2}$ and $d_{zx}(d_{yz})$, in the order of diminishing energy¹. The visible absorption in these systems is associated with the transitions from d_{zx} (d_{yz}) to d_{xy} (w_1), from $d_{x^2-y^2}$ to d_{xy} (w_2), and from d_{z^2} to d_{xy} (w_3), where w_1 is the shortest wave-length and w_3 the longest wave-length band with w_2 in between. The absorption spectra of square planar copper complexes in solution invariably consist of one broad absorption band in the visible region, which, however, could be resolved into three component bands by Gaussian analysis². With the