SHORT COMMUNICATIONS

TABLE I. Powder data for scorodite

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The high angle lines were not indexed because of the large number of possible indices.

The chemical, optical, and X-ray data show that the present mineral is the pure iron-arsenic end-member. This appears to be the first reported occurrence of scorodite in India.

Acknowledgements. The authors gratefully acknowledge the interest shown by Dr. M. V. N. Murthy in the present investigation. Our thanks are also due to Dr. B. Das Sharma for a preliminary spectrochemical analysis and for advice on the analysis.

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A. K. Datta
N. R. Sen Gupta

Reference

Allen (V. T.) and Fahey (J. J.), 1948. Amer. Min., vol. 33, p. 122.

[Manuscript received 9 August 1965]

The axial-ratio-inversion effect in Jahn-Teller distorted ML₆ octahedra in the epidote and perovskite structures

In field-free space, transition metal (M) ions have five degenerate (equal energy) d-electron orbitals, which split under the influence of an octahedral crystal field into three low energy (t₂g) and two high energy (e₅) orbitals. The t₂g orbitals are directed along the diad axes of the octahedron, i.e. between opposite pairs of ligand (L) ions, whilst
short communications

$e_g$ orbitals are directed along the tetrad axes, i.e. towards ligands, and the electrons in these orbitals are thus more strongly repelled.

When the symmetry of the assemblage of filled $d$-electron orbitals in any $M$ ion is lower than octahedral, the $ML_6$ group is distorted accordingly. This distortion (the Jahn–Teller effect) is strongest for ions with four (e.g. Cr$^{2+}$, Mn$^{3+}$) and nine (e.g. Cu$^{2+}$) $d$-electrons in the weak fields produced by $O^{2-}$ and $F^-$, and for our present purposes it is negligible for all other $M$ ions. The Jahn–Teller effect almost invariably makes itself felt as a tetragonal distortion of the octahedron with $c/a > 1$ (common) or $c/a < 1$ (rare). Other types of distortion have occasionally been recorded, but need not concern us here, as the purpose of this paper is to advance an explanation for the observation that Mn$^{3+}$O$_6$, Cr$^{2+}$F$_6$ and Cu$^{2+}$F$_6$ octahedra can be found in both the $c/a > 1$ and the $c/a < 1$ configurations.

Structural evidence. Recent work on epidote (Burns and Strems, unpub.) and viridine (Strens, unpub.) has shown that Mn$^{3+}$ replaces aluminium in tetragonally distorted AlO$_6$ octahedra in the epidote ($c/a = 0.95$) and viridine ($c/a = 1.12$) structures, and that these $c/a$ ratios are not greatly changed from their initial values (Ito et al., 1954; Burnham and Buerger, 1961) by this substitution.

X-ray investigations of the K$_2$CuF$_4$ (Knox, 1959) and KCuF$_3$ (Edwards and Peacock, 1959) structures have shown the CuF$_6$ octahedra to have $c/a < 1$, by contrast with the CuF$_2$ structure (Billy and Haendler, 1957) in which $c/a > 1$. Similarly, in KCrF$_3$ (Edwards and Peacock, 1959) $c/a < 1$, whilst in CrF$_2$ (Jack and Maitland, 1957) $c/a > 1$. Thus the Mn$^{3+}$O$_6$, Cr$^{2+}$F$_6$, and Cu$^{2+}$F$_6$ octahedra in different structures can be found in both $c/a < 1$ and $c/a > 1$ configurations, suggesting that the determining factor is, at least in part, structural.

Wave-mechanical calculations. Opik and Pryce (1957), Liehr and Ballhausen (1958), and Pryce et al. (1965) have made wave-mechanical calculations for isolated $ML_6$ systems, but none of these gives a definite answer concerning the relative stability of states with $c/a < 1$ and $> 1$, though there is general agreement that $c/a$ will increase with covalency. In the treatment of Pryce et al., the sign of a second-order term $\beta$ determines the stable configuration, and the following empirical relation is suggested for $\beta$:

$$\beta = |\text{const}| \left[ 1 - (|K_m - K_l|)/|\mu| \right],$$

where $|\mu|$ is a small number $\leq 3$, and $(K_m - K_l)$ is the electronegativity difference of the $M$ and $L$ ions.

Influence of covalency on $c/a$ for an isolated $ML_6$ system. Ideally, an
isolated ionic $ML_6$ system with negligible Jahn–Teller distortion has regular octahedral ($m3m = Oh$) symmetry with $c/a \equiv 1$. For $d^4$ ions ($Mn^{3+}$ and $Cr^{2+}$) with one unoccupied $d$ orbital the covalent component of the bonding is assumed to be $dsp^2$. For this special case the effect of covalency on $c/a$ is easily understood, since with increasing covalency

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

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\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]

\[ E_A - E_B \]

\[ c/a \approx 1 \]

\[ E_A - E_B \]

\[ c/a > 1 \]

\[ c/a < 1 \]
This structurally controlled inversion is referred to as the axial-ratio-inversion effect.

Application to known inverted structures. The between-chain AlO₅ octahedron in epidote (Ito et al., 1954) has c/a 0.95 when it is occupied by (Al, Fe)³⁺, neither of which ions gives rise to a Jahn–Teller effect or to square-planar bonding: this indicates that the site is compressed along its c axis, so that when Mn³⁺ enters the site the c/a < 1 configuration should be (and is) retained so long as \( E_A - E_B \) is not too large.

The remaining compounds showing axial ratio inversion belong to the perovskite (KCuF₃ and KCrF₃) and modified perovskite (K₂CuF₄) structures. In these compounds the c axes of the ML₆ groups are arranged parallel with the c axis of the crystal: this is to be expected, since disorder of the octahedral c axes would lead to severe local distortion of the structure, which would be energetically unfavourable. With this point established we can look for the factors favouring a short c dimension for the crystal, and thus for the ML₆ groups. We find that the face diagonal of the crystal (\( a/\sqrt{2} \) referred to an idealized cubic cell with a = \( \sqrt[3]{a/2c} \)) is approximately 5.9 Å for these compounds, compared with a radius sum 2(R₁ + R₂) of 5.3 Å. The K atom is thus 'loose' in its site, and contraction along c will give better packing than expansion. If the CrF₆ groups in KCrF₃ are imagined to be replaced by groups having the Cr-F distances observed in CrF₂, (c/a > 1), the expected volume change occurs:

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<th>c/a &lt; 1</th>
<th>c/a &gt; 1</th>
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<td>a Å</td>
<td>4.27</td>
<td>3.99</td>
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<tr>
<td>c Å</td>
<td>4.01</td>
<td>4.86</td>
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<td>V Å³</td>
<td>73.1</td>
<td>79.0</td>
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The increase in volume is probably associated with an increase in entropy, and if a polymorphic relationship should be found to exist between the hypothetical compound KCrF₃ (c/a > 1) and KCrF₃ (c/a < 1), the latter should be the low-temperature high-pressure form. This relationship should hold for most, if not all, possible polymorphs of this type. Replacement of K or F by larger ions should stabilize the c/a > 1 structure.

Conclusions. In isolated ML₆ groups, where M is a d⁴ or d⁹ ion, the c/a > 1 configuration should always be stable, and c/a should increase with covalency. In ionic crystals the c/a < 1 configuration is stable if the energy required to distort the crystal as a whole to accept octahedra with c/a > 1 rather than < 1 exceeds \( E_A - E_B \). The relative abundance of the two forms, and the confinement of the c/a < 1
distortion to ionic solids are thus explained. The failure of wave-mechanical treatments of isolated $ML_6$ systems to provide a satisfactory explanation of the $c/a < 1$ configuration in crystals is also understandable.

The possibility of polymorphism clearly arises in many structures containing tetragonally distorted octahedra: in general the structure with $c/a < 1$ has lower volume and entropy, and will be the low temperature high pressure form.

Acknowledgements. I should like to thank Dr. R. G. Burns, Dr. J. D. C. McConnell, and Dr. L. E. Orgel for reading and commenting on parts of the manuscript. Any remaining errors are mine alone. Financial support has been received from the Science Research Council.

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R. G. J. STRENS

References


[Manuscript received 19 September 1965]

Authigenic ferriferous aragonite from bottom sediments of the Adriatic sea

Petrographic analysis of sandy fractions of bottom sediments recently cored in the Gulf of Venice shows a high percentage of coarse carbonate constituents, consisting partly of rounded, detrital grains of limestone and dolomite (brought into the sea by Venetian rivers) and partly of irregular fragments, flat crusts, and occasionally rounded concretions of non-skeletal, micro-crystalline carbonates. These latter are usually yellowish to brownish in colour on account of the contaminating ferruginous material (Damiani, Favretto, Lenardon, and Morelli, 1964).