

TABLE I. Powder data for scorodite

<i>I</i>	<i>d</i>	$1/d^2$		<i>hkl</i>	<i>I</i>	<i>d</i>	$1/d^2$		<i>hkl</i>
		obs.	calc.				obs.	calc.	
vs	5.654 Å	0.0313	0.0315	111	w	2.324 Å	0.1852	0.1854	331
vwv	5.210	0.0368	0.0368	200	vwv	2.266	0.1948	0.1944	303
m	5.050	0.0392	0.0396	020	vwv	2.245	0.1984	0.1984	004
vvs	4.495	0.0494	0.0492	002	vwv	2.190	0.2085	0.2083	412
m	4.110	0.0592	0.0594	211	vwv	2.145	0.2173	0.2176	114
m	3.821	0.0685	0.0684	112	vwv	2.118	0.2229	0.2224	332
vwv	3.353	0.0889	0.0891	221	vwv	2.050	0.2380	0.2380	233
			0.0888	022	vwv	2.011			
vs	3.195	0.0980	0.0981	122	vwv	1.954	The high angle lines		
s	3.074	0.1058	0.1059	311	vwv	1.871	were not indexed be-		
s	3.013	0.1102	0.1107	131	vwv	1.846	cause of the large		
vwv	2.769	0.1304	0.1300	113	vwv	1.833	number of possible		
m	2.695	0.1377	0.1383	032	vwv	1.805	indices.		
s	2.601	0.1478	0.1472	400	vwv	1.760			
m	2.511	0.1586	0.1584	040					

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.

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ALLEN (V. T.) and FAHEY (J. J.), 1948. *Amer. Min.*, vol. 33, p. 122.

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The axial-ratio-inversion effect in Jahn-Teller distorted ML_6 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 (t_{2g}) and two high energy (e_g) orbitals. The t_{2g} orbitals are directed along the diad axes of the octahedron, i.e. between opposite pairs of ligand (*L*) ions, whilst

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 Strens, 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_2CuF_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.

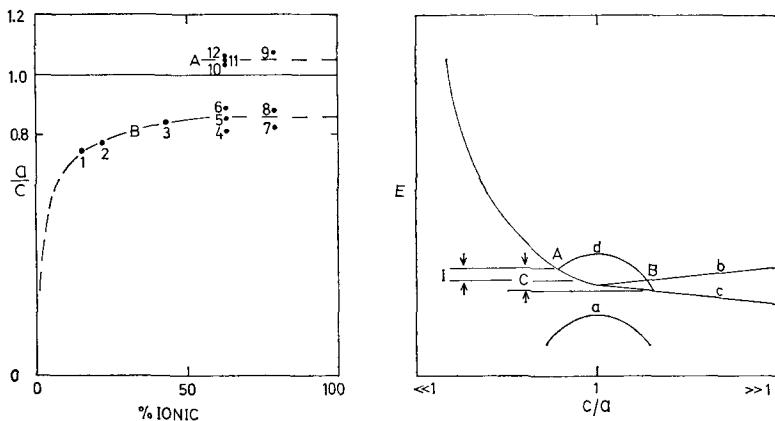
Wave-mechanical calculations. Opik and Pryce (1957), Liehr and Ballhausen (1958), and Pryce *et al.* (1965) have made wave-mechanical calculations for isolated ML_6 systems, but none of these gives a definite answer concerning the relative stability of states with $c/a < 1$ and > 1 , though there is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

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

where $|\mu|$ is a small number ≤ 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 ($m\bar{3}m = O_h$) 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



FIGS. 1 and 2: FIG. 1 (left). Relationship between $a:c$ ratio of ML_6 octahedra and covalency for some oxygen and halogen compounds of d^4 and d^9 ions. A, metastable branch on which fall compounds exhibiting the axial ratio inversion effect; B, stable branch with normal $a:c$ ratios. 1, $CuBr_2$; 2, $CuCl_2$; 3, $Cu_2Cl(OH)_3$; 4, Mn_2O_3 ; 5, CuF_2 ; 6, viridine; 7, CrF_2 ; 8, MnF_3 ; 9, $KCrF_3$; 10, piemontite; 11, $KCuF_3$; 12, K_2CuF_4 . FIG. 2 (right). Potential energy curve for the $M-L_z$ system. A Jahn–Teller energy term (a) is superimposed on the normal potential energy nuclear separation curves for ionic (b) and covalent dsp^2 (c) cases to give curve (d). Two minima are formed, one (A) at $c/a < 1$ is metastable, the other (B) at $c/a > 1$ is stable. $E_A - E_B$ is larger for the covalent (C) than for the ionic (I) case.

the bonds to the $L_{x,y}$ ligands strengthen, whilst those to the L_z ligands weaken, so that c/a increases from its minimum value of 1 to ∞ for 100% covalent bonding (fig. 1).

Influence of the Jahn–Teller effect. If we now superimpose on the potential-energy–internuclear-separation curve for the $M-L_z$ system a Jahn–Teller energy term, we obtain a curve with two minima (fig. 2), one (A) metastable, at $c/a < 1$, the other (B) stable at $c/a > 1$, separated by a maximum at $c/a \simeq 1$. In an isolated ML_6 group the $c/a > 1$ configuration should always be stable, but the $c/a < 1$ configuration will be stable in a crystal if the energy required to distort the structure from the $c/a < 1$ to the $c/a > 1$ configuration exceeds $E_A - E_B$.

This structurally controlled inversion is referred to as the axial-ratio-inversion effect.

Application to known inverted structures. The between-chain AlO_6 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 Mn^{3+} 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 (KCuF_3 and KCrF_3) and modified perovskite (K_2CuF_4) structures. In these compounds the c axes of the ML_6 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 ML_6 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 $2(R_F + R_K)$ 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 CrF_6 groups in KCrF_3 are imagined to be replaced by groups having the Cr-F distances observed in CrF_2 , ($c/a > 1$), the expected volume change occurs:

a	$c/a < 1$	4.27 Å	$c/a > 1$	3.99 Å
c		4.01		4.86
V		73.1 Å ³		79.0 Å ³

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 KCrF_3 ($c/a > 1$) and KCrF_3 ($c/a < 1$), 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 ML_6 groups, where M is a d^4 or d^9 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.

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References

- BILLY (C.) and HAENDLER (H. M.), 1957. Journ. Amer. Chem. Soc., vol. 79, p. 1049.
BURNHAM (C. W.) and BUERGER (M. J.), 1961. Zeits. Krist., vol. 115, p. 269.
EDWARDS (A. J.) and PEACOCK (R. D.), 1959. Journ. Chem. Soc., p. 4126.
ITO (T.), MORIMOTO (N.), and SADANAGA (R.), 1954. Acta Cryst., vol. 7, p. 53.
JACK (K. H.) and MATTLAND (R.), 1957. Proc. Chem. Soc., p. 232.
KNOX (K.), 1959. Journ. Chem. Phys., vol. 30, p. 991.
LIEHR (A. D.) and BALLHAUSEN (C. J.), 1958. Ann. Physics, vol. 3, p. 304.
OPIK (U.) and PRYCE (M. H. L.), 1957. Proc. Roy. Soc. A, vol. 238, p. 425.
ORGEL (L. E.), 1960. An introduction to transition metal chemistry, Methuen, London.
PRYCE (M. H. L.), SINHA (K. P.), and TANABE (Y.), 1965. Mol. Phys., vol. 9, p. 33.

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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).