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The Crystal Structure of $EuSO_4$ and $EuCO_3$

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The crystal structures of $EuSO_4$ and $EuCO_3$ have been studied by the powder diffraction method. The space group found for $EuSO_4$ is *Pnma* (D_{2h}^{16}) while for $EuCO_3$ it is *Pmcn* (*Pnma*) (D_{2h}^{16}). The orthorhombic lattice constants of $EuSO_4$ are $a = 8{\cdot}333$, $b = 5{\cdot}326$, $c = 6{\cdot}861$ Å, while those of $EuCO_3$ are $a = 5{\cdot}102$, $b = 8{\cdot}422$, $c = 6{\cdot}030$ Å. The radius of divalent europium is discussed.

Introduction

In the course of an investigation on the thermal decomposition of europium(III) oxalate, divalent europium compounds were obtained as intermediates (Glasner, Levy & Steinberg, 1963). These results have prompted the present X-ray study of europium(II) sulphate and europium(II) carbonate.

While no information was available on the structure of $EuCO_3$, some reported data on $EuSO_4$ (Pauling, 1937) showed it to be isomorphous with the corresponding barium and strontium salts.

Experimental and results

Preparations. The starting material was Eu_2O_3 from the Lindsay Co. (Code 1013, 99·9% pure). $EuSO_4$ was prepared by dissolving the oxide in hydrochloric acid and passing the solution through a Jones reductor into $8N$ H_2SO_4, following the method described in *Inorganic Syntheses* (Cooly & Yost, 1946).

Lemon yellow anhydrous crystals of $EuCO_3$ were obtained by digesting $EuSO_4$ in a 1:1 $NaOH + NaHCO_3$ solution (Cooly & Yost, 1946).

The densities of both compounds were measured by the pycnometric method, using benzene.

X-ray analysis of the powdered salts has been made by a General Electric Diffractometer with filtered Cu K radiation. Thin layers of the samples were spread out on microscope slides coated with petrola-

Table 1. *Lattice constants and densities of* $EuSO_4$, $EuCO_3$ *and the corresponding strontium salts*

Compound	Lattice parameters (Å)			Density (g.cm^{-3})	
	a	*b*	*c*	calc.	obs.
$EuSO_4$	8·333	5·326	6·861	5·409	5·44
	(8·46)	(5·37)	(6·90)	(5·22)	(4·99)
$SrSO_4$*	8·359	5·352	6·866		
$EuCo_3$	5·102	8·422	6·030	5·433	5·61
$SrCo_3$†	5·107	8·414	6·029		

* Swanson & Fuyat, 1953.
† Swanson, Fuyat & Ugrinic, 1954.

Table 2. *Calculated and observed* $Q_{hkl} = 1/d_{hkl}^2$ *and observed intensities*

$EuSO_4$				$EuCO_3$			
hkl	Q_c	Q_o	I_o	*hkl*	Q_c	Q_o	I_o
011	0·0565	0·0568	25	110	0·0525	0·0529	10
111	0·0709	0·0705	15	020	0·0564	—	—
201	0·0789	0·0787	10	111	0·0800	0·0803	100
002	0·0850	0·0847	20	021	0·0839	0·0840	40
210	0·0928	0·0928	100	002	0·1100	0·1100	15
102	0·0994	0·0993	25	121	0·1223	—	—
211	0·1141	0·1141	45	012	0·1241	0·1245	5
112	0·1347	0·1348	20	102	0·1484	—	—
020	0·1410	0·1410	15	200	0·1536	0·1538	10
301	0·1509	—	—	112	0·1625	0·1622	20
121	0·1767	0·1770	7	130	0·1653	overlapped	35
212	0·1779	—	—	022	0·1664		
220	0·1986	0·1984	7	211	0·1952	—	—
103	0·2057	0·2055	5	220	0·2100	0·2096	7
302	0·2146	—	—	040	0·2256	—	—
221	0·2199	0·2200	10	221	0·2375	0·2375	30
122	0·2404	overlapped	60	041	0·2531	0·2530	8
113	0·2409			202	0·2636	0·2638	15
203	0·2489	0·2495	30	132	0·2753	0·2753	20
				141	0·2915	—	—
				113	0·3000	0·2999	20
				023	0·3039	0·3036	20

tum, in order to reduce absorption of the radiation by the europous salts.

Diffraction patterns of $EuSO_4$ and $EuCO_3$ were indexed, and in both cases the unit cells were found to be orthorhombic. The lattice constants and densities are given in Table 1 and compared with the respective constants for the strontium salts. Pauling's values for $EuSO_4$ are also given in brackets. Calculated and observed $1/d^2$ values are given in Table 2; good agreement between these values has been obtained.

Further examination of the patterns shows that $EuSO_4$ is isomorphous with $SrSO_4$ and has the $BaSO_4$ structure type with space group *Pnma* (D_{2h}^{16}) and four molecules in the unit cell, while $EuCO_3$ has a KNO_3 type structure, the space group being *Pmcn* (*Pnma*) (D_{2h}^{16}), and four molecules in the unit cell.

Discussion

Comparison of the lattice constants of $EuSO_4$ found in this work with those obtained by Pauling shows that dimensions of the unit cell of $EuSO_4$ are somewhat smaller than reported by him. Pauling himself pointed out that there is some uncertainty in his results. On the other hand, as there is good agreement between the standard pattern and our measurements on $SrSO_4$, it may be assumed that there was no absorption error in our case to cause deviation of our results from those of Pauling. Moreover, the good agreement between the observed and calculated values of $1/d^2$, as well as of the density, leaves little doubt as to the reliability of the present results.

Crystal data of divalent europium compounds have been used by many authors to calculate the ionic radii of Eu^{2+}. Pauling, who found the lattice constants of $EuSO_4$ to be higher than those of $SrSO_4$, assumes the ionic radius of Eu^{2+} to be 1·17 Å (Sr^{2+} = 1·13 Å). Ketelaar also lists a somewhat higher value for the ionic radius of Eu^{2+} (1·14 Å) than for Sr^{2+} (1·10 Å) (Ketelaar, 1958). On the other hand, the lattice constants of the sulphide, selenide and telluride (Klemm & Senff, 1939) and the oxide (Eick, Baenziger & Eyring, 1956) of divalent europium, all with an NaCl type structure, were found to be slightly smaller than the lattice constants of the corresponding isomorphous strontium compounds. Hence the ionic radius of Eu^{2+} given by the above investigators is smaller by 0·03 Å than that of Sr^{2+}.

The lattice constants of $EuSO_4$ and $EuCO_3$ in the present work indicate that the ionic radii of Eu^{2+} and Sr^{2+} are equivalent, that of europium being somewhat smaller, certainly not larger, than that of strontium.

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A note on the determination of phases by anomalous dispersion.

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The differences which arise between the intensities $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$, when anomalously scattering atoms are present in a non-centrosymmetric unit cell, offer access to the phases of the reflexions. Two solutions, α_1 and α_2, are normally obtained for each independent reflexion and it appears to be customary to decide between these alternatives by adopting the value closer to the heavy-atom phase, α_H (see, *e.g.*, Dale, 1962; Hall & Maslen, 1964). While this undoubtedly selects the more probable phase for each reflexion it does not necessarily lead to the best electron-density distribution. To minimize the mean-square error in electron density each phase solution should be included with a weight proportional to the probability of its being the correct choice (*cf.* Woolfson, 1956; Dickerson, Kendrew & Strandberg, 1961).

It has been shown (Sim, 1959) that the probability of obtaining a value of $(\alpha - \alpha_H)$ between ξ and $\xi + d\xi$ is given by

$$p(\xi)d\xi = \exp(X \cos \xi)d\xi / 2\pi I_0(X) ,$$

where