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CRYSTAL STRUCTURE OF EUROPIUM TUNGSTATE

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CRYSTAL STRUCTURE OF EUROPIUM TUNGSTATE*

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The structure of europium tungstate, $\text{Eu}_2(\text{WO}_4)_3$, has been determined by single-crystal x-ray diffraction data. The crystals are monoclinic, space group $C2/c$, with $a = 7.676 \pm 0.003$, $b = 11.463 \pm 0.003$, $c = 11.396 \pm 0.005$ A, $\beta = 109.63 \pm 0.04^\circ$, $Z = 4$, $d_x = 7.37 \text{ g cm}^{-3}$. The atomic arrangement may be described as a scheelite superlattice with ordered vacancies in the cation positions, but atoms are displaced by considerable distances from the scheelite locations. Each W atom has four oxygen neighbors at average distances of 1.74 or 1.78 A. Some W atoms have a fifth neighbor at 2.19 A. Each Eu atom has eight oxygen neighbors at an average distance of 2.43 A.

* This work was done in part under the auspices of the U. S. Atomic Energy Commission.

Introduction

The rare earth elements form a series of isomorphous tungstates with the generic formula $R_2(WO_4)_3$, where R stands for a rare earth element, and some of these compounds have interesting fluorescence properties (MacDonald, Vogel and Brookman, 1962). We have investigated single crystals of the europium compound by x-ray diffraction and have determined the structure. The atomic arrangement is closely related to that of $CaWO_4$ (scheelite), and it may be described as a scheelite superlattice with ordered vacancies in the cation positions. Considerable distortions of the structure occur around these vacancies. These results may give an indication of the structure at defects in scheelite solid solutions.

Single crystals of the isomorphous compound $Ce_2(WO_4)_3$ were studied by Nelson and McKee (1946) who determined the unit cell and probable space group in agreement with our results.

Experimental

The synthesis of europium tungstate from europium oxide and tungstic acid and the growth of single crystals at temperatures near the melting point ($1130 \pm 15^\circ\text{C}$) has been described by MacDonald, Vogel and Brookman (1962). We had available single crystals up to several mm in size. Photographs of several crystals by Weissenberg and precession techniques established the symmetry and suggested the main features of the structure. The final results reported here are based on data from a crystal with dimensions approximately $0.11 \times 0.07 \times 0.06$ mm which was measured with the General Electric XRD-5 x-ray goniostat and $\text{MoK}\alpha$ radiation. Unit cell dimensions are based on $\lambda = 0.70929$ Å for $\text{MoK}\alpha_1$. Intensities were measured with a scintillation counter equipped with a pulse height discriminator for the 839 independent reflections permitted by the space group in the sphere with $\sin\theta/\lambda$ less than 0.596 ($2\theta < 50^\circ$); of these, 36 were assigned zero intensity. The data were corrected for absorption assuming that the crystal was a sphere with $\mu_r = 2.3$, according to the table given by Bond (1959). No correction was made for extinction. The limiting factors in the accuracy of the intensity data are extinction and the error in the absorption correction.

Calculations were made with the IBM-709 and IBM-7090 computers. The least-squares refinement was accomplished with a program written by P. K. Gantzel, R. A. Sparks and K. N. Trueblood, with minor changes. Atomic scattering factors for Eu^{+3} and neutral W (Thomas and Umeda, 1957) were modified for dispersion by adding -0.4 for Eu and -1.1 for W (Templeton, 1962). The imaginary dispersion term was neglected. Scattering factors for oxygen were estimated for $0^{-1/2}$ by interpolation in the tables of Ibers (1962).

Unit Cell and Space Group

The dimensions of the monoclinic unit cell of $\text{Eu}_2(\text{WO}_4)_3$ are:

$$a = 7.676 \pm 0.003 \text{ \AA}$$

$$b = 11.463 \pm 0.003$$

$$c = 11.396 \pm 0.005$$

$$\beta = 109.63 \pm 0.04^\circ$$

The corresponding dimensions reported for $\text{Ce}_2(\text{WO}_4)_3$ are $a = 7.68$, $b = 11.72$, $c = 11.51 \text{ \AA}$, $\beta = 109.8^\circ$ (Nelson and McKee, 1946, changed from kX and with a and c interchanged). These cells are very similar except for a five percent difference in volume in line with the lanthanide contraction. With four formula units ($\text{Eu}_2(\text{WO}_4)_3$) per unit cell, the density is calculated to be 7.37 g cm^{-3} . The density measured by MacDonald, Vogel and Brookman (1962) is 7.44 g cm^{-3} .

Reflections are systematically absent if $h+k$ is odd, showing that the lattice is C-centered. Reflections $h0l$ are absent if l is odd (or if h is odd), suggesting Cc and $C2/c$ as probable space groups. Morphological evidence and failure to detect a pyroelectric effect are cited by Nelson and McKee (1946) as indicating centric symmetry for the cerium crystals. The success of our structure determination with the assumption of a center of symmetry confirms $C2/c$ (C_{2h}^6) as the space group. Powder diffraction data show that $\text{Eu}_2(\text{WO}_4)_3$, $\text{Ce}_2(\text{WO}_4)_3$, and several other rare earth tungstates are isomorphous (MacDonald, Vogel and Brookman, 1962).

The lattice is pseudo-orthorhombic. A face-centered cell with double the volume of the one given above and which is called the "second setting" (Fig. 1) has dimensions:

$$a_2 = 7.676 \text{ \AA}$$

$$b_2 = 11.463$$

$$c_2 = 21.468$$

$$\beta_2 = 90.06^\circ$$

For this setting the space group symbol is $F2/d$. It is possible that the deviation of β from 90° is less than the experimental error, and this cell is convenient for the indexing of powder patterns. While the spot positions on the single crystal photographs fit an orthorhombic lattice, the monoclinic symmetry is clearly evident in the intensities. Twinning might be expected in this lattice with the result that the intensities would mimic orthorhombic symmetry, but no evidence of twinning was observed in any of the photographs.

Because the lattice is so nearly orthogonal, there exists a C-centered third setting (Fig. 1) which is easy to confuse with the first setting given above. It has the same a and b axes, but $c_3 = 11.403 \text{ \AA}$ and $\beta_3 = 109.73^\circ$. This c axis is $[\bar{1}0\bar{1}]$ in the first setting. If $\beta = 90^\circ$ for the face-centered setting, the two C-centered settings have identical dimensions. All subsequent discussion in this paper is in terms of the first setting.

Determination of the Structure

The structure was found by starting with the assumption, suggested by Dr. R. A. Pasternak, that it is related to that of CaWO_4 (scheelite). Scheelite is body-centered tetragonal (space group $I4_1/a$) with $a = 5.22$ and $c = 11.45$ Å (Sillen and Nylander, 1943). It was observed that a lattice similar to that of europium tungstate can be fitted to that of scheelite with its b axis corresponding to the c axis of scheelite and its a and c axes related to scheelite as shown in Fig. 1. Furthermore, the symmetry $C2/c$ is a subgroup of $I4_1/a$ when the lattices are related in this way and the origins are chosen in each case at the center of symmetry. The fact that europium tungstate is not orthorhombic in spite of its orthogonal lattice is understood when it is pointed out that there is no orthorhombic subgroup of $I4_1/a$.

The trial structure was obtained by transforming the coordinates of the atoms in scheelite to the monoclinic coordinate system. This process gives:

$$(0,0,0; 1/2,1/2,0) +$$

$4 W_1$ in (e): $\pm(0, y, 1/4)$ with $y = 1/8$.

$8 W_2$ in (f): $\pm(x, y, z; x, -y, z+1/2)$ with $x = 1/6, y = 3/8, z = 1/12$.

Calcium atoms are in the same positions with each y coordinate increased by $1/2$. If two-thirds of the calcium positions are occupied by europium atoms, they must be in the $8(f)$ positions. We chose the coordinates:

8Eu in (f) with $x = 1/3, y = 3/8, z = 5/12$.

The oxygen atoms in scheelite surround each tungsten atom at the corners of a tetrahedron. There are four distinct ways that these tetrahedra can be oriented in the monoclinic lattice which are equivalent to the scheelite structure. The one which most nearly resembles our final structure is shown

in Fig. 2. In any case, 48 oxygen atoms are located in the general sets 8(f) taken 6 times.

We attempted to refine this trial structure with least squares, first using only W and Eu atoms and about half of the data. The unreliability factor $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ was decreased quickly to 0.29. Introduction of oxygen atoms at the coordinates derived from scheelite for two of the distinct structures, after further refinement, achieved the same agreement with unrealistically large temperature factors. Introduction of oxygen atoms in certain other positions derived from a difference function gave no better results.

The initial shifts calculated by leastsquares from a structure like this with special coordinates often are unreliable because many terms with small or zero calculated structure factors may be assigned incorrect signs. Therefore we went back to only Eu and W atoms and arbitrarily reversed the initial shifts of some of the coordinates from the ideal structure. Experimentation with the x and z coordinates converged to another structure with $R = 0.45$.

An examination of the early calculations revealed that agreement was better in the layers with k even, and that for the h0l reflections R was 0.17. The agreement was especially bad for some reflections with large odd values of k. Simple calculations made obvious that the initial shifts in y were defective, and that the agreement would be improved by reversing these shifts.

The next refinement with half the data (low angles) reduced R from 0.28 to 0.18 in one cycle. Further cycles gave $R = 0.17$. A parallel refinement with the high-angle data gave $R = 0.15$ and nearly the same coordinates. In both cases the y coordinate of W_1 reversed its shift and went back to the direction achieved in the early calculations.

An electron density difference function (Eu and W atoms subtracted out) revealed a clear peak for each oxygen atom and peaks corresponding to anisotropic motion of each heavy atom. All other peaks were much smaller than an oxygen atom. This function was in striking contrast to the earlier difference function based on the incorrect heavy atom positions, which was a confusion of poorly shaped peaks.

Introduction of oxygen atoms with isotropic temperature factors for all atoms reduced R to 0.13 for 839 reflections. With anisotropic temperature factors for W and Eu atoms, R fell to 0.076 for 807 reflections with $(\sin\theta/\lambda)$ greater than 0.2. The resulting parameters are listed in Tables 1 and 2, and the observed and calculated structure factors are given in Table 3.

A further refinement with anisotropic temperature factors for all atoms gave negligible improvement and is not reported here.

The thermal parameters (Table 2) do not correspond to physically realistic thermal motion because of the negative values of β_{22} . These results show that the intensities for low k are weaker than they should be relative to those for higher k, probably because of insufficient correction for absorption. It is possible that extinction effects also contribute to this error. The similarity of the thermal parameters for the three heavy atoms suggests that the anisotropic refinement is mainly correcting for these effects in an empirical way rather than describing anisotropic thermal motion. Our objective in this work was to determine the atomic coordinates, which are not expected to be sensitive to these errors. A proper description of the thermal motion requires additional experimental work.

Discussion of the Structure

Europium tungstate is described as the scheelite structure with ordered vacancies, but the actual structure (Fig. 3) shows substantial distortions from the ideal structure derived from scheelite (Fig. 2). Atoms Eu and W_1 are within about 0.1 Å of the ideal positions, but W_2 is displaced about 0.5 Å. The largest distortions are in the oxygen positions. Four oxygen atoms surround each W_1 at the corners of a tetrahedron whose edges range in length from 2.73 to 3.11 Å. Each W_2 atom has four oxygen neighbors at the corners of a tetrahedron which is even more distorted. The distances of these four neighbors (Table 4) average 1.74 Å for W_1 and 1.78 Å for W_2 . A fifth oxygen neighbor is 2.19 Å from W_2 . If the coordination is considered to be five-fold, the coordination polyhedron is an irregular trigonal bipyramid, and pairs of these polyhedra share edges across centers of symmetry (Fig. 4). Bond angles at W_1 and W_2 are listed in Table 5.

These distortions of oxygen positions have no drastic effect on the environment of the Eu atom. It has eight oxygen neighbors at an average distance of 2.43 Å, and the individual distances (Table 4) differ by little more than the experimental error.

The oxygen coordinates in scheelite are not known with high accuracy. The coordinates proposed by Sillen and Nylander (1943) correspond to W-O distances of 1.75 Å and Ca-O distances of 2.41 and 2.52 Å, in close agreement with our results.

These results for $Eu_2(WO_4)_3$ show that the WO_4 groups are not rigid tetrahedra and suggest that it is more accurate to regard this substance as a double oxide than as a salt of tungstic acid.

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Table 1. Atomic coordinates, standard deviations, and isotropic thermal parameters.

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B^a
Eu	0.3338	0.3768	0.4066	0.0002	0.0001	0.0002	0.3 ^b
W ₁	0	0.1318	1/4	--	0.0002	--	0.4 ^b
W ₂	0.1452	0.3935	0.0507	0.0002	0.0001	0.0001	0.1 ^b
O ₁	0.161	0.045	0.221	0.004	0.003	0.003	1.0
O ₂	0.132	0.208	0.388	0.004	0.002	0.003	0.7
O ₃	0.222	0.320	0.195	0.003	0.002	0.002	0.4
O ₄	0.359	0.450	0.038	0.003	0.002	0.002	0.3
O ₅	0.053	0.459	0.423	0.004	0.002	0.003	0.8
O ₆	0.448	0.214	0.058	0.004	0.003	0.003	1.2

^aThe isotropic temperature factor is $\exp(-B\lambda^{-2}\sin^2\theta)$.

^bIsotropic parameter corresponding to the average anisotropic parameter (Table 2).

Table 2. Anisotropic thermal parameters.^{ab}

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Eu	220	-117	213	-2	-10	0
W ₁	143	-89	148	0	-56	0
W ₂	55	-117	201	13	-18	17

^aEach $\times 10^5$.

^bThese parameters in the temperature factor $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$ are those obtained by least squares. The cause of the negative values of β_{22} is discussed in the text. Obviously these values do not represent the actual thermal motion.

Table 4. Interatomic distances in $\text{Eu}_2(\text{WO}_4)_3$.^a

Atoms	Distance (A)	Atoms	Distance (A)
Eu-O ₁	2.42	W ₁ -O ₁ (2)	1.70
-O ₂	2.44	-O ₂ (2)	1.78
-O ₂	2.47		
-O ₃	2.36	W ₂ -O ₃	1.77
-O ₄	2.38	-O ₄	1.81
-O ₄	2.46	-O ₅	1.81
-O ₅	2.42	-O ₆	1.72
-O ₆	2.45	-O ₅	2.19

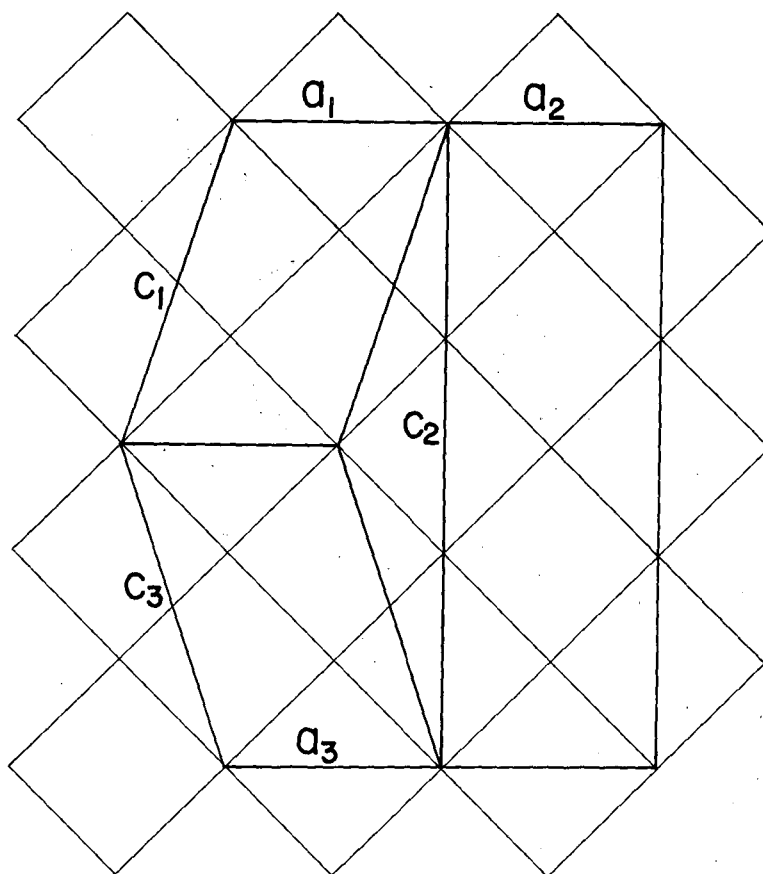
^aThe standard deviation is about 0.03 A for each distance.

Table 5. Bond angles.^a

Angles at W ₁			
O ₁ -W ₁ -O ₁	109°	O ₁ -W ₁ -O ₂	103°(2), 110°(2)
O ₂ -W ₁ -O ₂	121°		
Angles at W ₂			
O ₃ -W ₂ -O ₄	109°	O ₄ -W ₂ -O ₅	134°
O ₃ -W ₂ -O ₅	95°	O ₄ -W ₂ -O ₆	111°
O ₃ -W ₂ -O ₆	105°	O ₅ -W ₂ -O ₆	104°
O ₃ -W ₂ -O ₅ ' ^b	157°	O ₅ -W ₂ -O ₅ '	72°
O ₄ -W ₂ -O ₅ '	77°	O ₆ -W ₂ -O ₅ '	96°

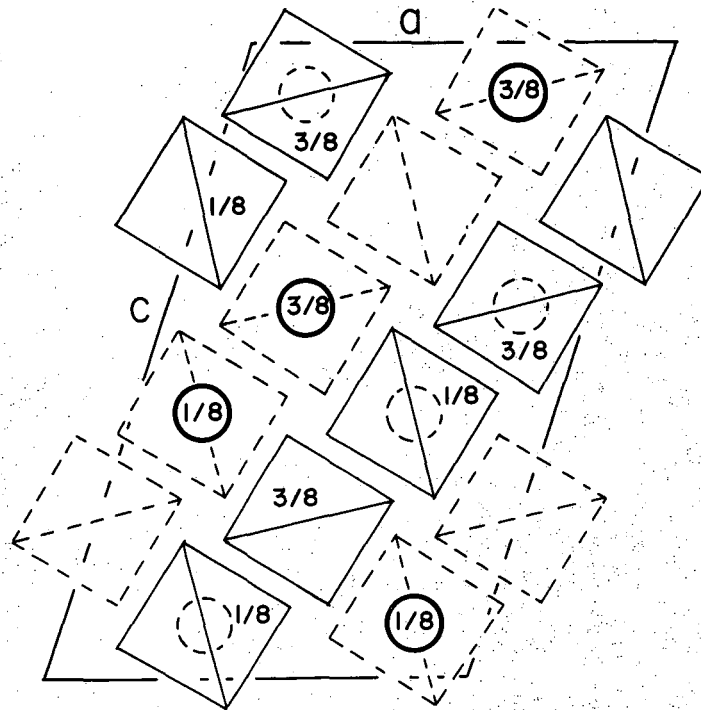
^a The standard deviation of each angle is 2° or less.

^b O₅' is the neighbor at 2.19 Å.



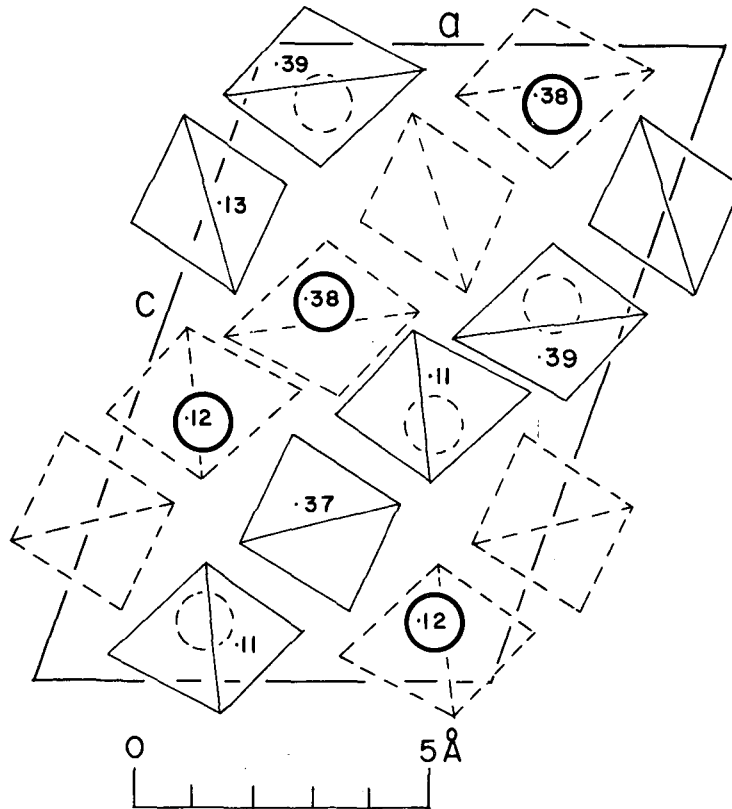
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Fig. 1. Relation of the unit cell of $\text{Eu}_2(\text{WO}_4)_3$ to the tetragonal lattice of scheelite. The subscripts on a and c refer to the three settings mentioned in the text.



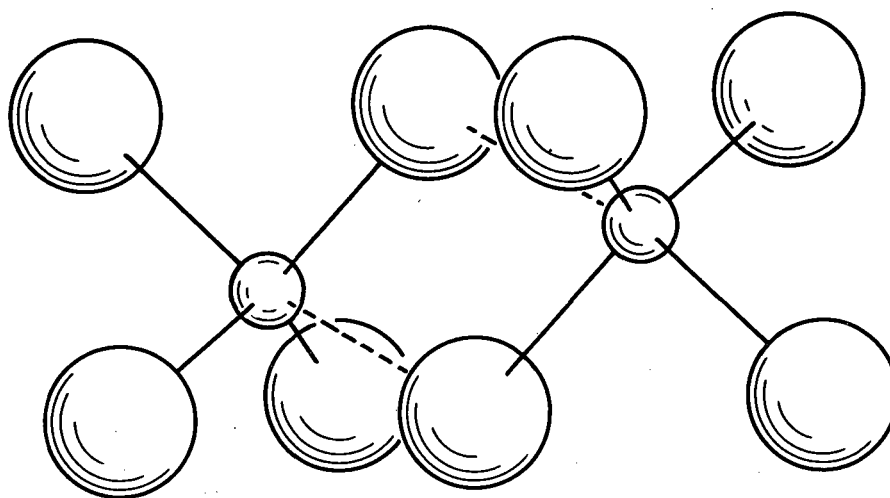
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Fig. 2. Ideal structure of $\text{Eu}_2(\text{WO}_4)_3$. The circles represent Eu atoms. The squares represent tetrahedra of oxygen atoms around each W atom. The numbers are y coordinates of the corresponding Eu or W atoms. The broken circles and squares represent Eu atoms and oxygen tetrahedra with y coordinates greater than $1/2$.



MU-27277

Fig. 3. Actual structure of $\text{Eu}_2(\text{WO}_4)_3$. Eu atoms and oxygen tetrahedra are represented as in Fig. 2.



MU-27278

Fig. 4. Oxygen neighbors of two W_2 atoms. The broken line indicates the neighbor at 2.19 Å.

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