THE STRUCTURE OF SKLODOWSKITE

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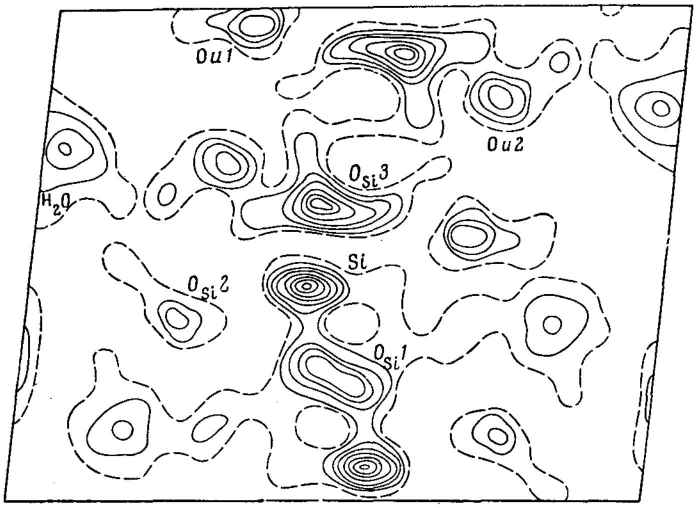
The first work on structure analysis of sklodowsite, $MgO \cdot 2UO_3 \cdot 2SiO_2 \cdot 7H_2O$, was published in 1959 [1], and there the reliability factor R, calculated for the h0l reflections (with $\sin\vartheta/\lambda \leq 0.6$), was equal to 0.22. The large value obtained for this factor can apparently be explained by the fact that, in a specimen of sklodowskite of cross section 0.05 × 0.07 mm with a linear coefficient of absorption of $\mu \approx 700$ cm^{-1}, no correction was made for absorption of x rays in the crystal. The author therefore undertook a further refinement of the sklodowskite structure, taking into account the absorption of x rays by the crystal.

The sample investigated was a crystal of prismatic shape with a cross section approximating a parallelogram of sides 0.03 × 0.07 mm. The axis of the prism was parallel to the b axis. Using a URS 50I diffractometer and Cu radiation, a set of I(h0l), intensities was obtained, and at the same time the h00 and 00l reflections were used to refine the a and c constants of the unit cell. In contrast to the previous values, it turned out that a = 16.89, c = 6.60 A, β = 96°20', or in the side-face-centered arrangement, a = 17.44 A, β = 105°46'. These results were confirmed by measurements on three other crystals.

Subsequently, for all the structure amplitudes F(h0l), Albrecht's method [2] was used to calculate the absorption corrections. The practical values of $\exp[-\mu(x_1 + x_2)]$ were determined using a slightly modified version of the graphical method of Rogers and Moffett [3], as follows: the crystal was divided up parallel to the ac plane into 84 parts, and two circles with series of closely-spaced parallel lines were used to determine, quite accurately, and without using additional apparatus, the directions of the incident and reflected beams at the centers of all the parts. The optimum number of divisions is not known, but too low a number leads to a distorted value of the absorption factor and only worsens the results.

Since the introduction of absorption corrections greatly increases the structure amplitudes for small Bragg angles, temperature corrections were introduced at the same time as the absorption corrections. The temperature factor B was equal to 2.5.

The electron density projection ρ (xz), and the difference projection (after subtraction of the U and Mg atoms) ρ_1(xz) (figure) constructed from the new values of F(h0l), agreed generally with the previously obtained [13] projection of ρ (xz). The most marked difference was a displacement of the peaks O_U 1



Difference projection of electron density of sklodowskite on the xz plane (uranium and magnesium atoms subtracted).

Coordinates of the Principal Atoms in the Structure of Sklodowskite (in the Body-Centered Arrangement)

Atom	x	y	z	Atom	x	y	z
U	0.257	0	0.120	$O_{Si}3$	0.235	0.187	0.44
Mg	0	0	0.500	O_u 1	0.155	0	0.035
Si	0.218	0	0.570	O_u 2	0.355	0	0.185
$O_{Si}1$	0.28	0	0.78	H_2O	0.020	0.21	0.30
$O_{Si}2$	0.128	0	0.627	×(H_2O)	0.08	0.500	0.82

and O_U 2 towards the uranium atom, i.e., a reduction in the uranyl distances. Other maxima were also slightly displaced. As before, the projection included the peak which was marked with a cross; it is suggested that this position may be occupied by the seventh water molecule (of the zeolite type). The new atomic coordinates for sklodowskite (in the body-centered arrangement) are shown in the table. The coordinates of the O_{Si} 3 atom, as before, were obtained from geometrical calculations and do not coincide with the coordinates of the O_{Si} 3 peak on the projection. This deviation from the experimental pattern is because, if the O_{Si} 3 atom is placed at the top of the corresponding peak, this leads to rather unsatisfactory distances in the SiO tetrahedron, and since the position of the O_{Si} 3 atom is difficult to establish accurately because of overlapping of the O_{Si} 3 and U peaks, we considered it justifiable to modify these coordinates to obtain better distances in the tetrahedron.

The reliability factor for the h0*l* reflection was calculated first from the uranium atom coordinates only, then by including the atoms U, Mg, Si, O_{Si} 2 and H_2O, and finally by including all atoms, giving values of 18.5, 16.5 and 15.5% respectively.

The U– Ou 1 and U– Ou 2 distances are now equal to 1.75 and 1.67 A, and the Si –O distances in the silicon tetrahedra to 1.61, 1.61, and 1.64A, with tetrahedron edges varying from 2.62 to 2.66A. The other distances are also slightly changed, while remaining within the permissible limits. The authors of [4] obtained equal distances for both uranyl oxygen atoms, equal to 1.70 A; they found Si– O distances in the SiO_4 tetrahedra varying from 1.70 to 1.76 A, and tetrahedron edges varying from 2.68 to 2.92 A.

In [1] it was suggested that the OH group replaces one of the oxygens of the uranyl group. In support of this proposal there is the increase in the corresponding U– O distance. There is, however, another possibility for replacement; the OH group might enter into the SiO_4 tetrahedron, replacing one of the four oxygen atoms. The formula of sklodowskite would then be $Mg[UO_2/SiO_4]_2 \cdot 5H_2O$, in complete agreement with Strunz's "Mineralogical Tables" [5].

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CRYSTAL STRUCTURES OF THE COMPOUNDS RIn_3 IN RARE EARTH METAL-INDIUM SYSTEMS

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Phase diagrams of the rare earth metal-indium systems have been established for La, Ce, and Gd. In these systems, together with other compounds, the compounds $LaIn_3$, $CeIn_3$, and $GdIn_3$ with structures of the $AuCu_3$ type [1, 2, 3, 5] have been found. Isostructural compounds are also known in the