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Abstract

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NEUTRON-DIFFRACTION STUDY OF THE CUBIC MODIFICATION OF PbF_2

The cubic (high-temperature) modification of PbF_2 is assigned to the structural type CaF_2 ([1]). However, an X-ray diffraction study is difficult in this case because of the large difference between the atomic amplitudes of fluorine and lead ($Z_F = 9$, $Z_{Pb} = 82$), and this conclusion is based mainly on crystallochemical analogies. In neutron diffraction the situation is more favorable, since the amplitudes of coherent nuclear scattering are $b_F = +0.55 \cdot 10^{-12}$ cm and $b_{Pb} = +0.96 \cdot 10^{-12}$ cm ([2]).

We carried out a neutron-diffraction study of cubic PbF_2, single crystals of which were grown in the laboratory of optical single crystals of the Institute of Crystallography, Academy of Sciences of the USSR.

Using a neutron diffractometer for the study of single crystals ([3]) and applying the method described in ([4]), we obtained, in all, 32 reflections from planes of the zones [100] and [110]. The diffraction pattern was recorded automatically on the chart tape of an electronic potentiometer during continuous slow rotation of the specimen and of the neutron detector (with preservation of the Bragg condition) in angular intervals encompassing the calculated positions of the diffraction maxima.

Table 1

Measured and calculated (without allowance for the temperature factor) intensities of reflections

hkl	I_{exp}	$L\Phi$	$L\Phi^*$	hkl	I_{exp}	$L\Phi$	$L\Phi^*$
111	73	40	12	622	0	0	0
200	3	0	0	444	40	50	61
220	100	100	122	711	14	12	2
311	36	21	6	551	12	12	2
222	0	0	0	640	0	0	0
400	65	70	86	553	15	12	2
331	34	17	5	800	35	47	57
420	0	0	0	733	12	12	2
422	53	60	73	820	0	0	0
511	20	14	4	644	0	0	0

hkl	I_{exp}	$L\Phi$	$L\Phi^*$	hkl	I_{exp}	$L\Phi$	$L\Phi^*$
333	21	14	4	822	32	47	57
440	46	54	66	660	33	47	57
600	0	0	0	555	8	14	2
442	0	0	0	662	0	0	0
620	48	50	61	840	28	47	57
533	12	12	2	911	9	12	2

To determine the diffraction intensities, the areas lying under the recorded count-rate curve were measured, with subtraction of the background level. The intensities measured in this way were reduced to the intensity of the primary neutron beam, which was monitored by a monitor···

counter. We estimate the relative error in measuring the intensities to be $\pm 5\%$ [(4)].

Table 1 gives the measured intensities and the values of $L\Phi$ and $L\Phi^2$ (reduced to an absolute scale [(5)]), calculated under the assumption of the CaF_2 structure with the coordinates of the basis atoms $Pb(0,0,0)$, $F_1(1/4,1/4,1/4)$, $F_2(3/4,3/4,3/4)$. Here $L = \dfrac{1}{\sin^2\vartheta}$ is the Lorentz factor, and the structure amplitude Φ_{hkl} for the given space group $Fm3m$ has the form

$$\Phi_{hkl} = \begin{cases} f_{\text{Pb}} + 2f_{\text{F}} & \text{for } h+k+l = 4n, \\ f_{\text{Pb}} & \text{for } h+k+l = 2n+1, \\ f_{\text{Pb}} - 2f_{\text{F}} & \text{for } h+k+l = 4n+2. \end{cases}$$

From consideration of these results it may be concluded that cubic PbF_2 does indeed have a fluorite-type structure. The close agreement of the experimental intensity values with the quantities $L\Phi$ indicates the predominantly dynamic character of the scattering, as was to be expected for the PbF_2 specimen used in the study (a sphere, $d = 8$ mm). Indeed, the discrepancy coefficient calculated on the assumption of a dynamic character of the scattering proves to be 20.3% (without allowance for the temperature correction!). If, however, a kinematic character of the scattering is assumed, the corresponding coefficient exceeds the above value by more than a factor of 2.

It is well known that X-ray analysis of crystal structures containing elements whose atomic numbers differ by approximately a factor of 10 is very difficult. The use of the neutron-diffraction method eliminates the difficulties associated with the poor detectability of a light atom in the presence of a heavy one. The contribution of F atoms to the intensities of reflections with a sum of indices that is a multiple of $4n$ even exceeds the contribution of the much heavier Pb atoms.

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Note: Figure translations are in progress. See original paper for figures.