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Vacancy Ordering in $Gd_{1-x}Se$

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Vacancy ordering is observed in the compound $Gd_{0.88}Se$. The symmetry is reduced from $Fm\bar{3}m$ for stoichiometric GdSe to $Pm\bar{3}m$ and the cubic cell edge is 5.7669(4) Å. The Gd occupancies become of Cu_3Au type, whereas no vacancies or distortions were observed for the Se sublattice.

Introduction

Stoichiometric GdSe crystallizes in the NaCl-type structure. The compound exists over a wide range of composition from $Gd_{1.08}Se$ to $Gd_{0.79}Se$ (*1*). Since the vacancy ordering of the cations is observed in the similar nonstoichiometric NaCl-type compounds $Sc_{1-x}S$, $Zr_{1-x}S$ and $Lu_{1-x}S$ (*2*), ordering of some kind is expected for $Gd_{1-x}Se$. The present study shows that vacancy ordering is indeed observed for $Gd_{0.88}Se$.

Experimental

Single crystals of $Gd_{0.88}Se$ were grown from the melt in sealed tungsten crucibles in an RF furnace. The crystals obtained showed a deep blue color and cleaved along {100}. Single-crystal and powder-diffraction studies revealed no apparent superstructure. Annealing the crystals under vacuum at 700°C for 1 week proved to be essential for the development of long-range ordering. During annealing, the color of the surface changed to a blue-grayish tinge, whereas the bulk retained the deep blue color. A fragment picked from the bulk material proved to be single crystalline, enabling us to perform an X-ray structure determination. The lattice is primitive cubic with a = 5.7669(4) Å, with space group $Pm\bar{3}m$ (No. 221). Graphite-monochromatized Mo$K\alpha$-radiation was used to collect 1994 reflections up to 60° 2θ on a Nonius CAD-4 diffractometer driven by the NRCCAD program (*3*). After a Gaussian-integration absorption correction, and merging of the

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symmetry-related intensities, 80 unique reflections were obtained, 45 of them with intensities greater than 2.5 counting-statistics sigmas. A first refinement of the NaCl-type substructure fixed the scale and extinction parameters for the subsequent refinement of the superstructure. The final residuals are $R_F = 0.022$ and 0.028, $wR_F = 0.022$ and 0.024, respectively, for the 45 observed and the 80 unique measured reflections. The refined occupancies gave a 0.88(1) Gd/Se atomic ratio, in agreement with the microprobe analysis (0.89(9)). All calculations were performed on a VAX-780 computer with the NRCVAX structure package (*4*). Crystal data are shown in Table I; observed and calculated structure factors are given in Table II.

Results and Discussion

In $Gd_{0.88}Se$, the observed superstructure is explained exclusively by the vacancy ordering at the Gd positions. The reduction of the symmetry from $Fm\bar{3}m$ to $Pm\bar{3}m$ without a change of cell parameters corresponds to an increase of the volume of the asymmetric unit by a factor 4. The order at the Gd positions is of the Cu_3Au type, with the Gd in the 1*a* position (0, 0, 0) having a lower occupancy than the one in the 3*c* ($\frac{1}{2}$, $\frac{1}{2}$, 0) position. The 3*c* position is not fully occupied either (see Table I). The occurrence of vacancies at both the 1*a* and 3*c* positions can be described as a mixture of two structures:

(a) a structure with $Fm\bar{3}m$ symmetry and uniform distribution of vacancies over all Gd sites, and

(b) a structure with $Pm\bar{3}m$ symmetry, with vacancies at the origin only, both with full occupation of the Se sites.

The refined occupation parameters correspond to a mixture of 0.85 of type a, with 9% Gd vacancies, and 0.15 of type b. Both the vacancy in type a and the proportion of type b allow for continuous stoichiometry within the overall space group symmetry $Pm\bar{3}m$, limited probably by strain effects and unfavorable charge distribution (*5*). In the case of NbO for example, the 1*a* cation vacancy is paralleled by a 1*b* anion vacancy (*6*). In $Gd_{0.88}Se$, the 1*b* and 3*c* anion positions are equally occupied, suggesting full occupancies. Displacements of the anions are forbidden by the fixed-coordinate special positions they occupy in $Pm\bar{3}m$ or would occupy in any primitive cubic space group with the observed cell parameters. However, it seems normal to expect some collapsing of the Se atoms around Gd vacancies. This can only occur with non-cubic symmetry, which was not observed here, or, retaining the cubic symmetry, by multiplication of the cell parameters. We therefore carefully searched for diffracted intensity outside the accepted reciprocal lattice nodes. We found only a barely significant reflection with reciprocal coordinates $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ and its equivalents in the cubic symmetry, indicating that the displacements of the Se atoms probably occur on a cubic cell with doubling of the *a* parameter. No other reflection could be observed, making the study of the Se displacements unfeasible.

TABLE I

CELL AND ATOMIC PARAMETERS OF $Gd_{0.88}Se$ (BLUE PHASE) (CUBIC CELL, SPACE GROUP $Pm\bar{3}m$ (NO. 221), $Z = 4$, $a = 5.7669(4)$ Å, Mo$K\alpha$ RADIATION, $\mu = 489$ cm^{-1}, $d_{calc} = 7.53$ g/cm^3, EXTINCTION COEFFICIENT 0.83(22))

Atom	Position	Occupancy	x	y	z	B_{iso}
Gd 1	1*a*	0.77(2)	0	0	0	0.10(40)
Gd 2	3*c*	0.92(1)	$\frac{1}{2}$	$\frac{1}{2}$	0	0.46(14)
Se 1	1*b*	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0.20(50)
Se 2	3*d*	1	0	0	$\frac{1}{2}$	0.21(16)

Note. The estimated standard deviations refer to the last digit printed.

TABLE II

STRUCTURE FACTOR TABLE FOR $Gd_{0.88}Se$

L	KFO	FC	SIG	L	KFO	FC	SIG	L	KFO	FC	SIG
	1,	0, L			4,	3, L		0	1744	1739	6
0	92	84	6	0	25	29	29		6,	1, L	
	1,	1, L		1	18	29	40*	0	13	16	67*
0	79	79	5	2	21	24	37	1	18	16	50*
1	770	782	3	3	7	20	120*		6,	2, L	
	2,	0, L			4,	4, L		0	1693	1663	6
0	2975	2992	12	0	1893	1824	6	1	4	12	213*
	2,	1, L		1	18	20	48*	2	1594	1592	6
0	67	68	6	2	1711	1739	6		6,	3, L	
1	65	65	7	3	9	12	106*	0	5	9	213*
	2,	2, L		4	1465	1527	6	1	6	9	153*
0	2736	2683	14		5,	0, L		2	16	5	65*
1	51	57	9	0	21	29	32	3	23	4	48*
2	2553	2462	20		5,	1, L			6,	4, L	
	3,	0, L		0	22	29	32	0	1460	1467	7
0	56	57	9	1	499	495	5	1	8	3	146*
	3,	1, L			5,	2, L		2	1384	1411	7
0	50	55	10	0	23	24	33	3	7	3	171*
1	664	655	4	1	17	24	46*		6,	5, L	
	3,	2, L		2	12	20	70*	0	13	3	97*
0	40	48	13		5,	3, L		1	5	1	241*
1	39	47	14	0	17	20	49*	2	18	5	71*
2	36	41	17	1	456	451	6		7,	0, L	
	3,	3, L		2	4	16	207*	0	5	5	199*
0	31	40	19	3	417	417	7		7,	1, L	
1	559	559	5		5,	4, L		0	5	6	210*
2	25	34	27	0	16	12	57*	1	384	389	7
3	515	495	6	1	4	13	210*		7,	2, L	
	4,	0, L		2	7	9	140*	0	10	3	104*
0	2223	2289	8	3	5	6	226*	1	5	4	215*
	4,	1, L		4	20	0	58*	2	13	0	80*
0	33	41	19		5,	5, L			7,	3, L	
1	33	40	19	0	16	6	65*	0	5	1	222*
	4,	2, L		1	388	389	7	1	360	365	8
0	2159	2146	14	2	14	4	77*	2	5	1	222*
1	29	34	23	3	341	365	7		7,	4, L	
2	2103	2024	7		6,	0, L		0	15	5	84*

Note. Columns are 10FO, 10FC, 100SIG; * for insignificant.

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