

Table 3. Calculated crystal-field parameters: point-charge (PCEM) and dipolar (ID) contributions; corrected parameters:  $ES(1 - \sigma_k) \langle r'^k \rangle / \langle r^k \rangle$

Experimental values are after Caro *et al.* (1979) and Souillat *et al.* (1972). Earlier calculations (Faucher *et al.*, 1980) are in parentheses.

Parameter (cm <sup>-1</sup> )	Nd <sub>2</sub> O <sub>3</sub>				Nd <sub>2</sub> O <sub>2</sub> S					
	PCEM	ID	PCEM + ID (ES)	ES(1 - $\sigma_k$ ) × $\langle r'^k \rangle / \langle r^k \rangle$	Experimental	PCEM	ID	PCEM + ID (ES)	ES(1 - $\sigma_k$ ) × $\langle r'^k \rangle / \langle r^k \rangle$	Experimental
B <sub>0</sub> <sup>2</sup>	-1541	-451	-1992	-580 (-575)	-836	-44	546	502	146 (207)	194
B <sub>0</sub> <sup>4</sup>	424	17	441	759 (754)	634	536	1	537	925 (1274)	912
B <sub>2</sub> <sup>4</sup>	1184	-21	1163	2002 (2092)	1606	798	11	809	1393 (1037)	924
B <sub>4</sub> <sup>0</sup>	283	-31	252	584 (590)	752	211	37	248	574 (595)	512
B <sub>4</sub> <sup>2</sup>	-169	-8	-177	-410 (-372)	-237	-139	3	-136	-315 (-320)	-300
B <sub>6</sub> <sup>0</sup>	261	12	273	632 (640)	672	205	-12	193	447 (484)	256

### 3. Discussion

The refined coordinates and cell parameters were used to recalculate *ab initio* electrostatic c.f.p. In Table 3 are reported for both compounds the point-charge distribution (PCEM), the induced-dipoles correction (ID), the total electrostatic parameters corrected for the shielding factor  $\sigma_k$  and the wave-function expansion, and the experimental c.f.p. as determined by Caro *et al.* (1979) for Nd<sub>2</sub>O<sub>3</sub> and Souillat *et al.* (1972) for Nd<sub>2</sub>O<sub>2</sub>S. Compared with our earlier work (Faucher *et al.*, 1980), the results of *ab initio* calculations for Nd<sub>2</sub>O<sub>3</sub> are not much changed since the 4 K structure is not significantly different from the room-temperature structure. Concerning Nd<sub>2</sub>O<sub>2</sub>S, the results are different since the coordinates of Ce<sub>2</sub>O<sub>2</sub>S (Zachariasen, 1949) were used previously. In fact, the coordinates of Nd<sub>2</sub>O<sub>2</sub>S at 4 K are very close to those of Ho<sub>2</sub>O<sub>2</sub>S (Boucherle *et al.*, 1979) and La<sub>2</sub>O<sub>2</sub>S (Morosin & Newman, 1973) at 300 K.

The dipolar correction to B<sub>0</sub><sup>2</sup> yields a sign and magnitude consistent with the experimental value. The influence of the dipolar corrections on higher-order c.f.p. is quite small while B<sub>0</sub><sup>4</sup> and B<sub>2</sub><sup>4</sup> are quite varied owing to changes in the point-charge contributions. However, one must conclude that the agreement between calculated and experimental c.f.p. is not significantly improved by the use of more accurate structural data; the origin of the observed discrepancies is

thus to be found in multipolar effects of higher order or a possible covalency contribution.

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**A neutron diffraction study of Cr<sub>3</sub>Si.** By J.-E. JØRGENSEN and S. E. RASMUSSEN, *Department of Inorganic Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark*

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### Abstract

Cr<sub>3</sub>Si, cubic, *Pm3n*,  $a = 4.5599$  (3) Å,  $Z = 2$ ,  $V = 94.8$  Å<sup>3</sup>,  $D_c = 6.448$  Mg m<sup>-3</sup>,  $\mu = 0.01048$  mm<sup>-1</sup>,  $R = 1.8\%$  for 21 reflexions [ $I > 3\sigma(I)$ ] and 4 parameters.  $U_{\text{iso}}^{\text{Cr}} = 0.0036$  (4) Å<sup>2</sup> and  $U_{\text{iso}}^{\text{Si}} = 0.0050$  (6) Å<sup>2</sup>.

Single crystals of Cr<sub>3</sub>Si have been grown by zone melting in our laboratory (Jørgensen & Rasmussen, 1979). Cr<sub>3</sub>Si has

the A15 or  $\beta$ -tungsten structure and many intermetallic compounds with this structure are high-temperature superconductors. Several A15 compounds, *e.g.* V<sub>3</sub>Si (Batterman & Barrett, 1964), exhibit a cubic to tetragonal phase transition at low temperature. Cr<sub>3</sub>Si has no superconduction transition down to 0.015 K (Blaugher, Hein, Cox & Waterstrat, 1969) and neutron powder diffraction experiments at room temperature and 6 K (Jørgensen, 1979) showed that Cr<sub>3</sub>Si remains cubic at low temperature. A neutron diffraction

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experiment was carried out in order to estimate the quality of the crystals grown by zone melting. A crystal of dimensions  $2 \times 2 \times 2$  mm was cut out of a bigger crystal which was later used for inelastic neutron scattering. The crystal is in this way representative for the whole preparation. The crystal used in this experiment was mounted on a Hilger Ferranti automatic four-circle diffractometer at the DR3 reactor at Risø. A total of 186 reflexions distributed over the eight octants were measured up to  $\sin \theta/\lambda = 0.76 \text{ \AA}^{-1}$ . The  $\omega$ - $2\theta$  scan mode was employed. The data were reduced as follows: The peak profiles were reduced to  $F^2$  values using the  $\sigma(I)/I$  criterion (Lehmann & Larsen, 1974). Lorentz and absorption corrections were made. Symmetry-related reflexions were averaged leading to an internal consistency factor of 5.3% on  $F$ . 21 independent reflexions with  $I > 3\sigma(I)$  were used in the least-squares refinement. The crystal was mounted on an aluminium rod. Scattering from aluminium accounts for the small intensity ( $5\sigma$ ) observed for the 422 and 500 reflexions, of which 500 is space-group forbidden. The intensities were corrected for thermal diffuse scattering (TDS). All phonons for which the plateau in the TDS profile was smaller than the width of the Bragg peak were included in the TDS correction. This was of little significance as the crystal is hard and so the neutron velocity was smaller than the sound velocity. The elastic constants,  $c_{11} = 5.3 \times 10^{11}$ ,  $c_{12} = 2.8 \times 10^{11}$  and  $c_{44} = 1.3 \times 10^{11} \text{ N m}^{-2}$ , used in the TDS correction were estimated from phonon data on  $\text{Cr}_3\text{Si}$  (Jørgensen, Axe, Corliss & Hastings, 1982). Neutron scattering lengths (3.52 fm for Cr and 4.2 fm for Si) were taken from *International Tables for X-ray Crystallography* (1962), and the lattice constant  $a = 4.5599(3) \text{ \AA}$  was determined by X-ray diffraction (Jørgensen & Rasmussen, 1979). The following computer programs were used: *PROCH*, *DATAPP*, *DSORTH*, *LINEX* (State University of New York at Buffalo crystallographic computer programs), and a TDS correction program (Merisalo & Kurittu, 1978). The results of different refinements are shown in Table 1.\*

From Table 1 it is seen that anisotropic refinement does not improve the  $R$  value significantly. Corrections for extinction were made in the Zachariassen (1967) approximation and the stronger reflexions have up to 53% extinction. The integrated intensities are not very much affected by TDS because  $\text{Cr}_3\text{Si}$  is a fairly hard material. An X-ray investigation of  $\text{Cr}_3\text{Si}$  (Staudenmann, 1977) gave  $U_{11} = 0.00329(3)$  and  $U_{22} = 0.00375(3) \text{ \AA}^2$  for Cr and  $U = 0.00391(4) \text{ \AA}^2$  for Si.

\* Lists of structure factors and TDS correction parameters ( $\alpha$ ) have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36348 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Refinement of room-temperature data on  $\text{Cr}_3\text{Si}$*

21 independent reflexions are used in each refinement on  $F$ . (a) Refinement without TDS correction. (b), (c) Anisotropic and isotropic refinements with TDS correction. Neutron wavelength = 1.07  $\text{Å}$ . (d) From an X-ray investigation of  $\text{Cr}_3\text{Si}$  (Staudenmann, 1977). Positions: Cr:  $\frac{1}{4}, 0, \frac{1}{2}$  and Si: 0,0,0.

	(a)	(b)	(c)	(d)
Scale factor	740 (13)	740 (10)	750 (14)	
Cr: $U_{11} (\text{Å}^2)$		0.0038 (8)		0.00329 (3)
$U_{22} (\text{Å}^2)$		0.003 (1)		0.00375 (3)
$U_{22} (\text{Å}^2)$	0.0031 (4)		0.0036 (4)	
Si: $U_{\text{iso}} (\text{Å}^2)$	0.0045 (6)	0.0050 (6)	0.0050 (6)	0.00391 (4)
Extinction ( $\times 10^{-4}$ )	11 (1)	11 (1)	11 (1)	
$R_w(F)$	1.7	1.8	1.8	
$R_w(F^2)$	2.6	2.5	2.6	

Our data indicate that the crystal investigated has a good crystal perfection and that the crystal is ordered and stoichiometric.

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