

PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 53, NUMBER 5

1 FEBRUARY 1996-I

BRIEF REPORTS

Brief Reports are accounts of completed research which, while meeting the usual Physical Review B standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Structural study on the high-pressure phase strontium III

Markus Winzenick and Wilfried B. Holzapfel

Fachbereich Physik, Universität GH Paderborn, D-33095 Paderborn, Germany

(Received 26 July 1995)

Improvements in energy dispersive x-ray diffraction with synchrotron radiation together with a specially modified diamond anvil high pressure cell result in more detailed data for the previously observed complex high pressure phase Sr III extending the range of observed lattice spacings from 75–600 pm. Together with the measured intensities these data are best described by an orthorhombic body-centered lattice with the lattice parameters $a=561.7(6)$ pm, $b=571.8(6)$ pm, and $c=305.4(3)$ pm at ambient temperature and 31.3 GPa with 4 atoms in this unit cell represented by the space group *Imma* with the atoms located on the position $4e$ and the free atom parameter $z=0.125(25)$.

INTRODUCTION

The discovery of many unusual structures in the heavier alkaline earth metals Ca, Sr, and Ba under pressure^{1,2} has stimulated not only further experimental studies³ but also many theoretical activities which show that these phenomena can be explained by $s \rightarrow d$ electron transfer in the conduction bands of these “pretransition” metals under pressure.⁴ Most successfully theoretical calculations reproduced at first the systematic structural changes from the cubic face centered (*cF4*) to the cubic body centered (*cI2*) structure around 20 GPa for Ca, 3.5 GPa for Sr and (theoretically) at small negative pressures for Ba.^{5–7} (Pearson symbols for the structures will be used throughout this paper following the recent recommendation by IUPAC (Ref. 8) and keeping in mind that this nomenclature reveals more readily structural relations for more complex and less commonly encountered structures.) At intermediate pressures, where the $s \rightarrow d$ transfer leads to unusual structures in the *IIa* metals, the experimental and theoretical studies have by far not yet solved all the problems. Only recently the experimental observation of a *cP1* phase for Ca (Ref. 9) at ambient temperature and pressures above 32 GPa was confirmed by theoretical calculations¹⁰ together with the prediction of a *hP2* structure at pressures slightly in excess of the experimental studies covering the range to 50 GPa. For Sr and Ba the situation is much more complex and none of the previous studies could

solve the structures for Sr III, Sr IV, Sr V, and Ba IV, only a strong similarity for the pattern of Sr V and Ba IV was noted so far.⁹ Due to the progress of structural stability calculations with first principle methods in recent years^{10,11} these more complex structures offer now a special challenge for both theoretical and experimental studies.

EXPERIMENTAL DETAILS

The high pressure phase Sr III which is stable between 28 and 38 GPa was studied by energy dispersive x-ray diffraction (EDXD) in HASYLAB with synchrotron radiation. Details of the EDXD station in HASYLAB have been given previously.¹² The experiments were performed with different diamond anvil cells (DAC). In contrast to previous EDXD measurements with a conventional DAC (Ref. 13) with sintered tungsten carbide backings for the diamonds offering an open diffraction cone of $2\Theta < 12^\circ$ some of the present experiments were performed also with a modified version of this DAC using a B_4C backing for one of the diamonds to open the diffraction cone up to $2\Theta = 30^\circ$. With this modification also the recently developed spinner for this DAC (Ref. 14) could be applied to reduce possible effects from texture. Mineral oil was used as pressure transmitting medium around the sample in the central hole of an inconel gasket. During the preparation the highly reactive sample was always protected by the oil against oxidation. The ruby

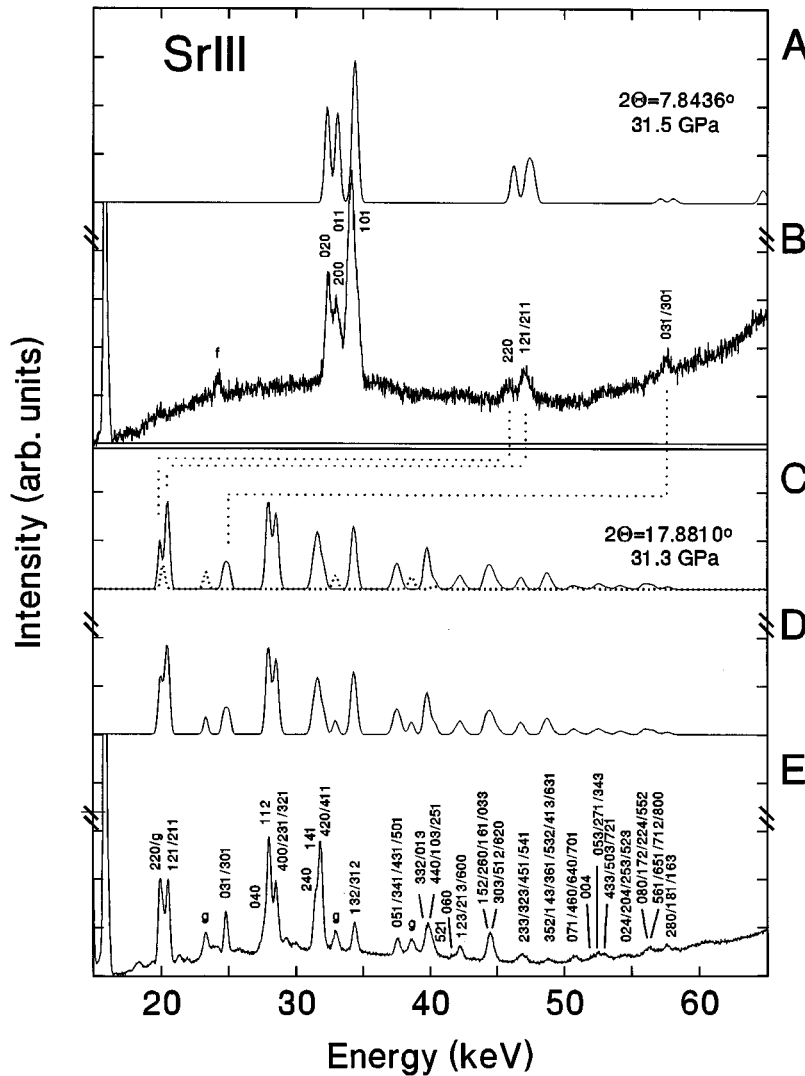


FIG. 1. Observed and calculated EDXD pattern of *oI4*-Sr III for different diffraction angles 2Θ . The dotted lines connect the same diffraction lines in the section (a)+(b) and (c) to (e). (a) Calculated EDXD pattern for an *Imma* structure of Sr III at 31.5 GPa. (b) Observed EDXD pattern of Sr III for the standard diffraction angle of $2\Theta = 7.8436^\circ$ at 31.5 GPa and room temperature. The pattern was recorded by rotating the sample with a spinner to reduce possible texture. A fluorescence line from the detector is marked by “f.” (c) Calculated EDXD pattern for Sr III at 31.3 GPa. Contributions from the gasket material are indicated by the dotted curve. (d) Sum of the calculated pattern for Sr III and gasket. (e) Observed EDXD pattern for Sr III with indexing for an *Imma* structure recorded with the enlarged diffraction angle $2\Theta = 17.8810^\circ$ at 31.3 GPa and room temperature. “g” marks the diffraction lines from the gasket material.

fluorescence technique with the nonlinear pressure scale¹⁵ was applied for pressure determination. Several experiments were carried out at room temperature with different diffraction angles of $2\Theta = 6^\circ, 8^\circ, 10^\circ$, and 18° to observe all the diffraction lines between 60 and 600 pm. Recording times for the x-ray patterns ranged from 30 to 120 min depending on the complexity of the pattern.

RESULTS AND DISCUSSION

Different diffraction patterns for Sr III at almost the same pressure but for different diffraction angles are shown in Figs. 1(b) and 1(e). The correspondence between the diffraction lines observed at different angles is indicated in Figs. 1(b) and 1(c) by dotted lines. The tests for indexing the pattern included cubic, hexagonal, tetragonal, and orthorhombic systems with up to 8 atoms per unit cell, as well as the monoclinic system with up to 4 atoms per unit cell. Only one orthorhombic body centered lattice with $a = 561.7(6)$ pm, $b = 571.8(6)$ pm, and $c = 305.4(3)$ pm and 4 atoms per unit cell gives satisfactory results which corresponds to a reasonable volume decrease of 1.6(9)% for the II–III phase transition around 28 GPa. The axes of this *oI4* unit cell were

labeled according to the standard crystallographic setting.¹⁶

A detailed structural analysis of the diffraction data showed systematic extinctions compatible only with the three space groups *Imma*, *Ima2*, *I2₁2₁2₁*. Since many of the atomic arrangements within these possible structures are identical for an elemental solid and many others are energetically unfavorable, the unit cell with the highest symmetry given by the space group *Imma* with the atoms on the positions $4e$ and one free parameter $z \sim 0.125(25)$ remained as the best fitting structure for the intensity pattern presented in Fig. 1. The two parts of Fig. 1, 1(a)+1(b) and 1(c) to 1(e), show patterns for different diffraction angles, in which the parts 1(a)+1(b) present the diffraction lines for d spacings between 140 to 600 pm and the parts C to E for $60 \text{ pm} < d < 250 \text{ pm}$. The comparison between observed and calculated intensities shows the best fit for $z \sim 1/8$. Minor deviations for the intensities of the strongly overlapping lines, e.g., 240/141/420/411 can be attributed within the experimental uncertainties to small effects from texture and/or to minor uncertainties in the d spacings for these unresolved lines.

A detailed comparison of observed and calculated d spacings for the present structural assignment is presented in Table I for one diffraction pattern taken with the diffraction

TABLE I. Comparison between experimental and calculated d spacings for $oI4$ -Sr III at 31.3 GPa from EDXD pattern recorded with $2\Theta=17.8810^\circ$. d spacings marked with stars are values observed in different pattern for $2\Theta=7.836^\circ$. Calculated d values which are not resolved by the present technique are related by straight lines to the corresponding experimental values.

d (obs.)/pm	d (calc.)/pm	Diff./pm	hkl	d (obs.)/pm	d (calc.)/pm	Diff./pm	hkl
285.1*	285.9	+0.8	020		88.4		611
280.0*	280.8	+0.9	200		85.5	+0.4	233
269.1	269.4	+0.3	011	85.1	85.4	+0.3	323
269.1	268.3	-0.8	101		85.2	+0.1	451
200.7	200.4	-0.3	220		84.9	-0.2	541
194.5	195.6	+1.1	121	81.7	82.2	+0.5	352
194.5	194.4	-0.1	211		82.0	+0.3	143
160.9	161.7	+0.8	031		81.8	+0.1	361
160.9	159.6	-1.3	301		81.7	+0.0	532
143.9	143.0	-0.9	040		81.6	-0.1	413
142.4	142.7	+0.3	112		81.0	-0.7	631
140.0	140.4	+0.5	400	78.6	78.9	+0.3	071
140.0	140.1	+0.2	231		78.9	+0.3	460
139.4	139.4	-0.6	321		78.3	-0.3	640
127.0	127.4	+0.4	240		77.6		701
125.4	126.2	+0.8	141	76.4	76.3	-0.1	004
	126.0	+0.7	420	76.0	76.0	+0.0	053
	124.5	-0.9	411		76.0	+0.0	271
116.1	116.6	+0.5	132	75.3	75.8	-0.2	343
	115.9	-0.2	312		75.7	+0.3	433
106.2	107.1	+1.0	051		75.4	+0.1	503
	106.5	+0.3	341	74.9	-0.4	721	
	106.0	-0.1	431	73.2	73.8	+0.6	024
	105.4	-0.7	501		73.7	+0.5	204
100.0	100.5	+0.5	332	73.4	+0.2	253	
	100.2	+0.2	013	72.9	-0.3	523	
	100.2	+0.2	440	70.9	71.5	+0.6	080
	100.2	+0.2	103		71.4	+0.5	172
	100.1	+0.1	251		71.3	+0.4	224
98.9	98.9	+0.0	521		71.0	+0.1	552
95.6	95.3	-0.4	060		70.7	-0.2	561
94.5	94.5	+0.0	123	70.5	-0.4	651	
	94.4	-0.1	213	70.5	-0.4	712	
	93.6	-0.9	600	70.2	-0.7	800	
89.6	90.3	+0.7	152	69.2	69.3	+0.1	280
	90.2	+0.6	260		69.1	-0.1	181
	89.8	+0.2	161		69.0	-0.2	163
	89.8	+0.2	033				
	89.4	-0.2	303				
	89.4	-0.2	512				
	89.4	-0.2	303				
	89.0	-0.6	620				

angle of $2\Theta=17.8810^\circ$ corresponding to a measurable range of d values from 285 to 69 pm. The indexing of the lines shows thereby a standard deviation between observed and fitted d values of less than 0.5% and for some weaker overlapping lines maximum deviations below 1%. The arrangement of the atoms in the $oI4$ structure of Sr III is illustrated in Fig. 2. For a comparison with the β -tin structure the origin of the unit cell is shifted in this figure with respect to the standard representation. For $a=b$ this structure is the same as β tin. Therefore the $oI4$ structure for Sr III can be considered as a small orthorhombic distortion of the β -tin structure. A similar $oI4$ structure with a significantly different value for the atomic position parameter z has been assigned to one high-pressure phase of Si observed as an intermediate phase between the $tI4$ (β -tin) phase Si II and the $hP1$ phase Si V.¹⁷ The value of $z=0.2$ for this structure reflects a tendency of layer formation and more open packing in comparison with the β -tin structure, whereas Sr III is more closely related to β tin with only minor orthorhombic distortions. In comparison with recent first principle calculations for the

different high-pressure structures of Ca, the present data can offer now additional stimulation for similar calculations on the high-pressure behavior of Sr also from the point of view that this low symmetry structure for Sr III should be supported by theoretical results.

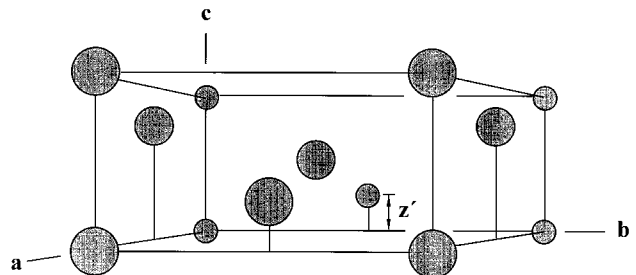


FIG. 2. Perspective view of the atomic arrangement for Sr III in the proposed $oI4$ structure. With respect to the standard setting the origin of the unit cell is shifted in this figure for better comparison with the β -tin structure which results in the corresponding atomic position parameter $z'=2z$.

ACKNOWLEDGMENTS

We would like to thank F. Porsch for valuable discussion, W. Sievers for the technical assistance, and J. Otto for taking

care of the beam line. Financial support by the German Ministry of Research and Technology (BMFT) with Contract No. 05 5PPAXB is gratefully acknowledged.

-
- ¹D. A. Young, *Phase Diagrams of the Element* (University of California Press, Berkeley and Los Angeles, CA, 1991).
- ²H. Olijnyk, Ph.D. thesis, Universität GH Paderborn, 1985.
- ³K. Takemura, *Phys. Rev. B* **50**, 16 239 (1994).
- ⁴J. C. Duthie and D. G. Pettifor, *Phys. Rev. Lett.* **38**, 564 (1977).
- ⁵H. L. Skriver, *Phys. Rev. B* **31**, 1909 (1985).
- ⁶J. A. Moriarty, *Phys. Rev. B* **8**, 1338 (1973).
- ⁷J. A. Moriarty, *Phys. Rev. B* **34**, 6738 (1986).
- ⁸International Union of Pure and Applied Chemistry, *Nomenclature of Inorganic Chemistry*, Recommendations 1990 (Blackwell Scientific Publication, Oxford, 1990).
- ⁹H. Olijnyk and W. B. Holzapfel, *Phys. Lett.* **100A**, 191 (1984).
- ¹⁰R. Ahuja, O. Eriksson, J. M. Wills, and B. Johansson (unpublished).
- ¹¹J. Hafner, *Static and Dynamics of Alloy Phase Transformations* (Plenum, New York, 1994).
- ¹²W. A. Grosshans, E. F. Düsing, and W. B. Holzapfel, *High Press. Res.* **6**, 169 (1991).
- ¹³G. Huber, K. Syassen, and W. B. Holzapfel, *Phys. Rev. B* **15**, 5123 (1977).
- ¹⁴F. Porsch (unpublished).
- ¹⁵H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
- ¹⁶E. Parthé and L. M. Gelato, *Acta Crystallogr.* **40A**, 169 (1984).
- ¹⁷M. I. McMahon and R. J. Nelmes, *Phys. Rev. B* **47**, 8337 (1993).