

Seven-Fold Coordinated MgSe at 202 GPa

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Energy-dispersive x-ray diffraction studies at the Cornell High Energy Synchrotron Source were made to 202 GPa on MgSe which was found to undergo a phase transformation from the rocksalt to the seven-fold coordinated FeSi (or AuBe) structure with new peaks clearly evident at 99 GPa and internal position parameters continuing to change to the highest pressure. This is the first phase transition observed in the three magnesium chalcogenides which have the rocksalt structure at atmospheric pressure (MgSe, MgS and MgO) and may have important implications for transitions of MgO and MgS. The internal atomic positions u and w were accurately obtained as a function of pressure. This is the first accurate determination of internal atom positions above one megabar and above two megabars. The equation of state over the entire range obeyed a Birch equation with $B_0 = 62.8 \pm 1.6$ GPa and $B_0' = 4.1 \pm 0.1$.

[rocksalt to Fe-Si transition, seven-fold coordination, distorted rocksalt, internal atom position by EDX, equation of state]

1. Introduction

The strontium, barium and calcium chalcogenides transform from the six-fold coordinated B1 to the eight-fold coordinate B2 structure at high pressure (except for BaO which transforms first to the NiAs structure and then to the quasi-eight PH_4I phase. There is simple correlation between this transformation pressure and the ratio of the anion to cation radius as shown in Figure 1 [1-3]. Also shown from this correlation is the predicted pressure where a transition to an eight-fold CsCl structure might be expected to occur for the Mg and Be compounds (assuming no other transformation occurs instead). For the magnesium chalcogenides this expected transformation pressure is around 202 GPa while for the beryllium chalcogenides it is around 1 TPa. With this in mind a study of MgTe and MgSe was begun. It was found that at atmospheric pressure MgTe existed both as the wurzite and nickel arsenide structure and that the B8, NiAs, phase was the more stable, and persisted at high pressure [4], consistent with calculations [5,6]. In the ideal B8 phase of MgTe, the magnesium atom is surrounded by eight equidistant atoms, six tellurium atoms and two magnesium atoms, while the tellurium is surrounded by six equidistant atoms of magnesium. Such a B8 structure could be said to be seven-fold coordinated on the average. As noted by Luo et al. [7] this is a very stable phase and will probably have to be taken to substantially higher pressure (than indicated by Figure 1) to reach the B2 phase. MgSe has the B1 structure at atmospheric pressure. At high pressure we found that a transformation to the Fe-Si [8] or Be-Au [9] structure occurs. This motivated theoretical calculations on this B28 structure [10]. We subsequently made more thorough studies to 202 GPa, and accurately measured the internal atom positions as a function of pressure.

2. Results and Discussion

The Au-Be structure of MgSe is characterized by a simple cubic lattice with a basis of four selenium ions at $uuu, (1/2)+u, (1/2-u), \bar{u}\bar{u}, (1/2+u), (1/2-u), (1/2-u)\bar{u}, (1/2+u)$ and four magnesium ions at $www, (1/2+w), (1/2-w), \bar{w}\bar{w}, (1/2+w), (1/2-w), (1/2-w)\bar{w}, (1/2+w)$. When $u = 0$ and $w = 1/2$ the structure is the six-fold B1 or NaCl structure with a nearest interion distance $r = a/2$. The ideal Fe-Si structure is exactly seven-fold coordinated for

each element. This occurs when $u = (3 - \sqrt{5}) / 8 = 0.095492$, $w = 0.404508$, and $r = 0.5352a$ i.e. with a 7.04% increase in interatomic distance relative to the B1 crystal of the same volume. The space group of the Fe-Si or Au-Be structure is $T^4 - P2_13$ (#198). Table 1 shows data at 202 GPa including the experimental values of the lattice spacings and intensities and the corresponding calculated fit for $u = 0.0828$. Figure 2 shows the variation of Bragg R_p vs u (for best w 's at each of the u 's). There is a sharp minimum at $u = 0.0828$. The corresponding

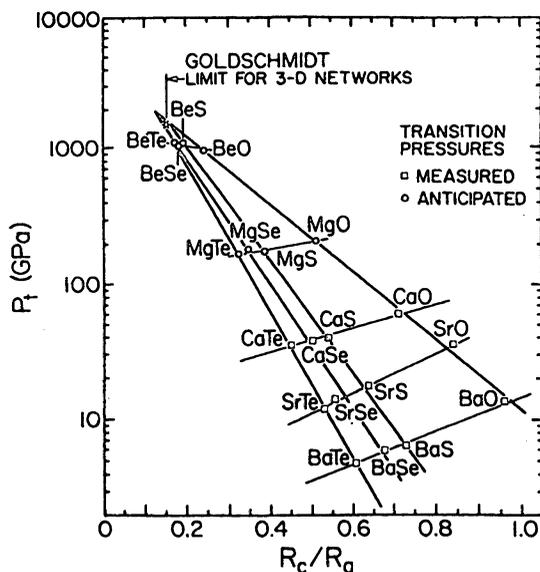


Fig. 1. Six-fold to eight-fold transition pressures versus the ratio of the cation radius to the anion radius (after Ref. 1 which was an extension of work in Refs. 2 and 3). The solid black squares represent experimental data, the open circles represent empirically expected transition pressures to 8-fold (if no other transition intervenes).

Table 1. Diffraction data for the B28 phase of MgSe at 202 GPa. I_{calc} is based on $u=0.0828$ and $w=0.4173$. The energy-interplanar spacing product was $Ed=32.490$ keV-Å. The energy at CSR was 5.28 GeV. The fitted lattice parameter is 4.3082Å. $V/V_0=0.491$.

hkl*	$d_{\text{obs}}(\text{Å})$	$d_{\text{calc}}(\text{Å})$	I_{obs}^{**}	I_{calc}
200	2.142	2.154	17.2	20.0
210	1.928	1.927	100	100
211	1.771	1.759	56.8	47.6
220	1.505	1.523	8.9	7.5
221	1.429	1.436	31.6	30.9
310	1.363	1.362	9.8	16.5
311	1.284	1.299	20.7	8.9
222	--	1.244	--	4.7
320	1.193	1.195	11.4	9.6
321	1.154	1.151	52.7	51.1
400	--	1.077	--	3.7
410,332	1.044	1.045	24.0	15.2

*h00 with h_{odd} has zero intensity in this structure.

**At this diffraction angle the 110 and 111 peaks are on the shoulder of the K_{α} and K_{β} fluorescence peaks of Se. At smaller angles the intensities of these peaks can be quantitatively measured.

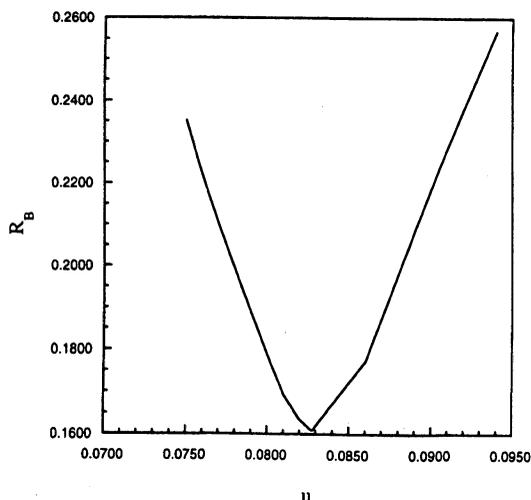


Fig. 2. Variation of R_B vs u for MgSe at 202 GPa. This is based on all possible peaks from 200 through 410.

This represents the first accurate determination of internal atom positions above one megabar (100 GPa). It should be noted that this determination was made by energy-dispersive x-ray diffraction. The limitation in this case was due to broad peak widths caused by strain broadening and, perhaps, by transformation broadening. The former limitation could be removed by use of a hydrostatic medium such as helium. If transformation

broadening is small, then the inherent peak width $\text{FWHM} = 0.145 \sqrt{E(\text{keV})/5.9}$ of the germanium detector would apply. If that becomes a limitation, then it is expected that in the future the germanium detector would be replaced by an advanced version of the bolometer, an early version being described elsewhere [11].

Inasmuch as the DAC was rotated about its axis [12], the sampling of different crystal orientations is identical to that obtained with an image plate in angular dispersive studies. Thus it would appear that ADX will have little if any inherent advantage over EDX for internal atom position determination in the near future.

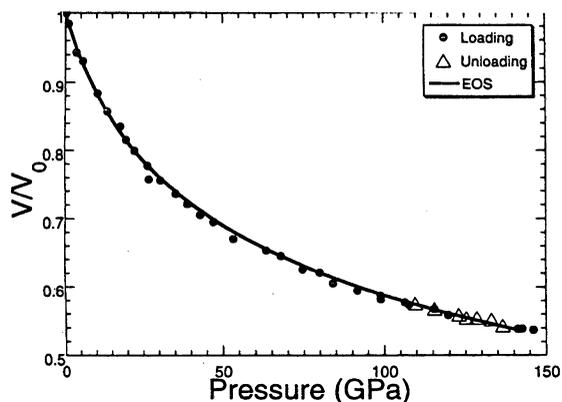


Fig. 3. Fractional volume vs pressure. The data is fitted to a Birch equation [13] with $B_0 = 62.8$ GPa and $B_0' = 4.1$.

The variation of u with P is described in Reference 12. Figure 3 shows the fractional volume versus pressure, obtained using a Pt marker. Results in a subsequent experiment were obtained with only the sample present; the sample was then used as an x-ray marker with the previously determined equation of state. There is no noticeable evidence for a volume discontinuity. It appears that the phase transition involves a X_5^- instability [14]. Recent theoretical calculations motivated by our work have been presented in this conference [15]. The results are in fairly close agreement.

Inasmuch as the six-fold B1 to seven-fold B28 transition occurred prior to the expected B1 to eight-fold B2 transition at 180 GPa (see Figure 1), it seems likely that a transition to eight-fold coordination (or quasi-eight-fold coordination), if it occurs, will be delayed to a substantially higher pressure. It seems likely that similar behavior will occur in MgS and MgO, so that the eventual transitions in these materials to eight-fold or approximately eight-fold coordinations might occur at much higher pressures than Figure 1 suggests.

Acknowledgments

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ago at a Workshop in Daresbury, "Is EDX likely to go the way of the horse and buggy?"

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References

- [1] C. Narayana, V.J. Nesamony and A.L. Ruoff, submitted for publication.
- [2] K. Syassen, *Phys. Stat. Solidi*, **91**, 11 (1985).
- [3] S. Ekbundit, A. Chizmeshya, R. La Violette and C.H. Wolf, *J. Phys. Cond. Matter*, **8**, 8251 (1996).
- [4] T. Li, H. Luo, R.G. Greene and A.L. Ruoff, *Phys. Rev. Lett.*, **74**, 5232 (1995).
- [5] C.Y. Yeh, Z.W. Lu, S. Froyen and A. Zunger, *Phys. Rev. B*, **46**, 10086 (1992).
- [6] P.E. Van Camp and V.E. Van Doren, *Int. J. Quantum Chem.* **55**, 339 (1995).
- [7] H. Luo, K. Ghandehari, R.G. Greene, A.L. Ruoff, S.S. Trail and F.J. DiSalvo, *Phys. Rev. B*, **52**, 7058 (1995).
- [8] L. Pauling and A.M. Soldate, *Acta Cryst.*, **1**, 212 (1948).
- [9] B.D. Cullity, *Trans. AIME*, **171**, 396 (1947).
- [10] P.E. Van Camp, V.E. Van Doren and J.L. Martins, *Phys. Rev. B*, **55**, 775 (1997).
- [11] D.A. Wollman, G.C. Hilton, K.D. Irwin and J. Martinis, in *Proceedings of Microscopy and Microanalysis*, ed. by G.N. Bailey, J.M. Corbett, R.V.W. Dimlich, J.R. Michael and N.J. Zaluzec, San Francisco Press, SF (1996), p. 488.
- [12] A.L. Ruoff, A. Ho, M. Pai and C. Narayana, submitted for publication.
- [13] J.F. Birch, *J. Geophys. Res.*, **83**, 1257 (1978).
- [14] H.T. Stokes and D.M. Hatch, *Isotropy Subgroups of the 230 Crystallographic Space Groups*, World Scientific Pub. Co., New York (1988).
- [15] P. Van Camp and V. Van Doren, this conference.