

Phase transformation of BeS and equation-of-state studies to 96 GPa

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We report the existence of a reversible first-order phase transition of BeS from the zinc-blende structure, *B3*, to the nickel-arsenide structure, *B8*, at 51 GPa with a volume change of 11%. The NiAs phase remains stable up to at least 96 GPa. A second-order Birch equation describes the equation of state of the *B3* phase with $B_0 = 105$ GPa and $B'_0 = 3.5$. Preliminary studies of BeO to 66 GPa are described. [S0163-1829(97)07346-3]

I. INTRODUCTION

Among the chalcogenides of the Group IIA elements (Be, Mg, Ca, Sr, Ba), BeS, BeSe, and BeTe crystallize at room pressure and temperature in the fourfold-coordinated cubic zinc-blende (ZB) structure. The remainder have the sixfold-coordinated NaCl structure, except for BeO and MgTe; BeO has the wurzite structure and MgTe has the nickel-arsenide structure.¹

It has been found that the NaCl structure of Ca, Sr, and Ba transform to the eightfold-coordinated CsCl structure² except for BaO that transforms to a distorted CsCl structure. It has been pointed out in the case of the alkali hydrides and halides that the transformation pressure varies rapidly in a homologous series in which the cation changes while the anion is constant but the transformation pressure varies much less in a homologous series in which the anion changes while the cation is constant.³ This behavior is clearly exhibited by the Ca, Sr, and Ba compounds as shown in Fig. 1. The dependence on the ionic radius ratio was first shown in part by Syassen⁴ and expanded by Ekundit *et al.*⁵ The references for the individual data points are given in the legend of Fig. 1.³⁻¹⁴ (In the case of BaO, the pressure at which it transformed to a distorted CsCl structure was used.) Figure 1 shows the expected transition pressures to eightfold coordination for the MgX chalcogenides and for the BeX chalcogenides based on this radius ratio criteria. The asterisk shows the Goldschmidt radius ratio of 0.155 that is the dividing point between two-dimensional structures and three-dimensional structures. It is of interest that the lines nearly come together at a common vertex of 0.155. The pressure anticipated from Fig. 1 to reach eightfold coordination in the BeX chalcogenides is in the TPa range (1000 GPa) and in the MgX chalcogenides is in the neighborhood of 200 GPa.

The BeX chalcogenides differ substantially from the others because of their small ionic radius ratio. They therefore have fourfold coordination. They also are more covalent. The Phillips ionicities range from only 0.169 in BeTe to 0.312 in BeS.¹⁵ These BeX compounds have similar structure and bonding to the Group III-V semiconductors. In particular they have large band gaps (2.7–5.5 eV), high bulk moduli, and the lattice constants of BeSe and BeTe are close to those of GaAs and ZnSe.¹⁶ The III-V compounds primarily transform to the NaCl structure or β -Sn structure or to orthorhombic structure,¹⁷⁻¹⁹ but recently it was found that AIAs and AIP transform to the NiAs structure.^{19,20} Typically

these transitions in the III-V compounds involve a 17% volume decrease at the fourfold to sixfold transition. In MgTe, the volume decrease from the metastable wurzite structure to the NiAs structure is 22%.²¹ In BeTe and BeSe the decrease is 11.5%.² No transition has been observed in BeO that has the wurzite structure at atmospheric pressure. The present paper presents results of studies on BeS to 96 GPa. The major results of this study include the determination of the crystal structure of the high-pressure phase and the equation of state. This study is a part of our investigation of the structural properties of the Group II-VI and III-V compounds at high pressure.

II. EXPERIMENTAL

A. Sample

The BeS was purchased from Alfa Aesar (Johnson-Matthey). It had a purity of 99%. X-ray-diffraction studies

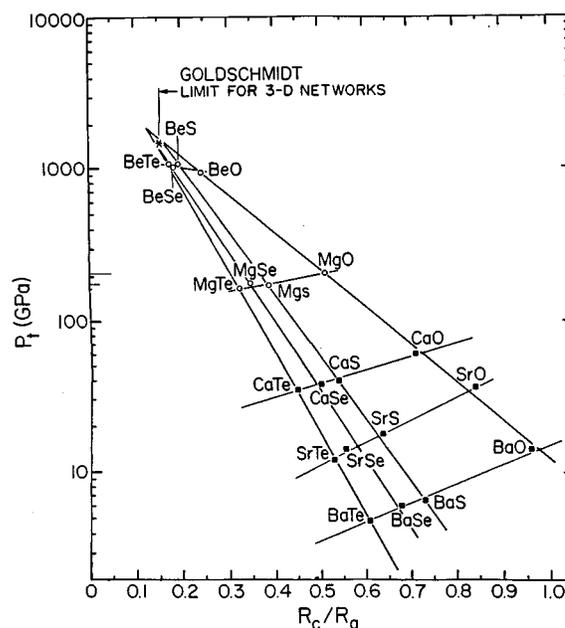


FIG. 1. Pressure vs the cation radius to the anion radius. Note the near convergence to the point at 0.155 that divides 2D and 3D structures. Experimental results are from the following references: BaTe (Ref. 6), BaSe (Ref. 7), BaS (Ref. 8), BaO (Refs. 8 and 9), SrTe (Ref. 10), SrSe (Ref. 11), SrS (Ref. 4), SrO (Ref. 12), CaTe, CaSe, and CaS (Ref. 13), CaO (Ref. 14).

showed only the zinc-blende peaks of BeS. The sample had a light gray color and was opaque.

B. DAC and EDXD measurements

Diamond-anvil cells (DAC's) were used to generate pressure. The sample was ground into a fine powder in a dry box and loaded into the DAC. In the first experiment a small amount of gold was placed in the center region of the sample and this was used to determine pressure. The pressure was determined by the isothermal equation of state of gold obtained from shock-wave experiments.²² Diamond anvils with 200 μm diameter flat tips were used in the first experiment. The tungsten gasket was preindented from 250 μm thick to 80 μm thick and the sample hole had a diameter of 75 μm . In the second experiment diamond anvils with 450 μm diameter flat tips were used. The 250 μm -thick stainless steel gasket was preindented to 80 μm thick and then a 300 μm hole was drilled. This was filled with 0.1 μm diamond powder and epoxy. Then a 150 μm diameter sample hole was drilled in the cured composite. This composite ring kept the sample thicker, which was helpful for studying these low Z materials. No pressure medium was used, so the state of stress was nonhydrostatic.²³ We do not know the yield strength of BeS, so we could not make a correction to the lattice parameter of the sample due to nonhydrostatic pressure.²³ The corrected equation of state (EOS) is expected to be somewhat softer.⁵ The measurements of the first experiments suffice to obtain the equation of state and the structure of the new phase. However, it was decided to make a second study with no marker material since the sample itself could now serve as the marker. In this case, apparently because the sample in the DAC had not been clamped sufficiently in the dry box, BeO peaks appeared in the spectrum (BeS reacts with H_2O vapor to form BeO). Ordinarily, we would have dropped this experiment, but because of the shortness of time at the Cornell high energy synchrotron source, and the fact that the peaks of BeO fortuitously did not interfere with the peaks of BeS at atmospheric pressure, we continued. The results show that it is possible to study two different materials simultaneously.

Energy dispersive x-ray-diffraction (EDXD) experiments were performed at the Cornell high energy synchrotron source at room temperature.

III. RESULTS

The lattice constant of BeS at 1 atm measured by this work is 4.870 \AA compared to an earlier value of 4.865 \AA . In the first experiment new peaks began to appear at 59 GPa and the transition was soon complete; the new NiAs phase persisted to the highest pressure, 96 GPa. During unloading the peaks of the ZB phase began to reappear at 43 GPa.

In the second experiment, the transition began at 66 GPa and fractured upon further increase of the load precluding making the unloading study.

Figure 2 shows the P - V behavior. The data of the ZB phase were fitted to the second-order Birch equation of state²⁴

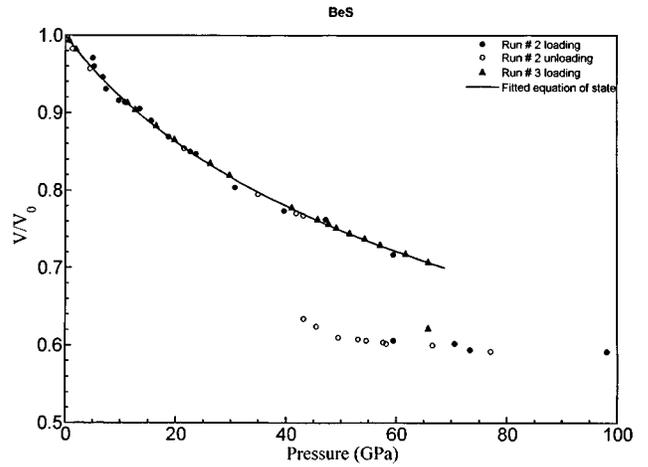


FIG. 2. P - V behavior of BeS.

$$P = \frac{3}{2} B_0 \left\{ \left(\frac{V_0}{V} \right)^{7/3} - \left(\frac{V_0}{V} \right)^{5/3} \right\} \times \left[1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V_0}{V} \right)^{2/3} - 1 \right] \right], \quad (1)$$

where P is the pressure, V/V_0 is the volume fraction, B_0 is the bulk modulus at zero pressure, and B'_0 is the derivative of the bulk modulus with respect to pressure at zero pressure. We find $B_0 = 105$ GPa and $B'_0 = 3.5$.

Figure 3 shows the diffraction pattern at 0.6 GPa. The results for the ZB phase of BeS are summarized in Table I. The theoretical intensity ratios are obtained as described elsewhere;²⁵ the assumption of a sample thickness approaching zero was shown to be justified. The agreement of the d spacings is very good. We note that in Fig. 3, a diamond peak is present. In this case, a diamond powder-epoxy composite formed a ring around the sample and the diamond peak appeared because the beam apparently slightly overlapped this ring.

Disagreements with intensities based on the assumption of a random distribution of orientation of equiaxed grains with ideal mosaic structure can occur because of texturing

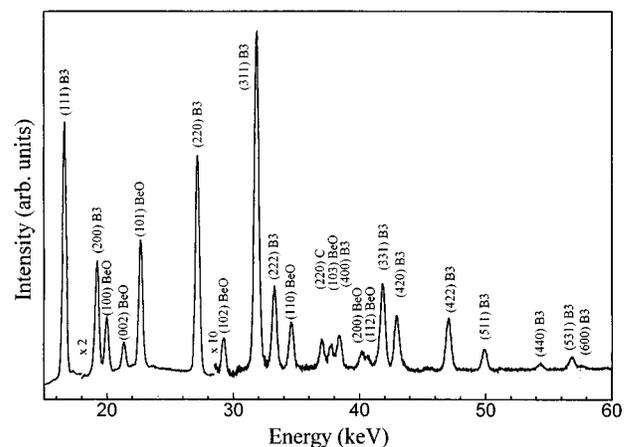


FIG. 3. The x-ray-diffraction pattern at 0.6 GPa for the BeS (B3) BeO (B4) mixture. $Ed = 46.685$ keV \AA . CESR energy at 5.28 GeV.

TABLE I. List of the observed interplanar spacings and relative intensities I of BeS at 0.6 GPa along with the theoretical corresponding values based on the zinc-blende structure. The fitted lattice parameter is 4.860 Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was $Ed=46.685$ keV Å without $\mu_{\text{COH corr.}}$.

hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
111	2.806	2.806	100	100
200	2.431	2.430	22.6	36.0
220	1.718	1.719	48.1	40.7
311	1.466	1.466	16.0	26.3
222	1.404	1.403	3.8	4.33
400	1.216	1.215	1.6	2.90
331	1.116	1.115	4.2	4.72
420	1.087	1.087	2.7	2.46
422	0.992	0.992	2.8	2.72
511+333	0.936	0.935	1.1	1.24
440	0.859	0.859	0.34	0.41

(the orientations are not random), stacking faults resulting from growth or deformation (deformation occurs in a diamond-anvil cell especially when the sample serves as the pressure medium), the sample size from which diffraction occurs is small so that not enough crystals are present to assure randomization of orientation even though a larger aggregate of the sample has random orientation. The temperature effect on the peak height will be relatively small because of the large bulk modulus (105 GPa). The temperature effect is expected to be smaller than in GaAs (Ref. 25) whose bulk modulus at $P=0$ is 75 GPa.

Table II shows the results for the $B4$, wurzite phase, of BeO at 0.6 GPa. The intensities are computed for the internal

TABLE II. List of the observed interplanar spacings and relative intensities I of BeO at 0.6 GPa along with the theoretical corresponding values based on the wurzite structure. The fitted lattice parameters are $a=2.697$ Å and $c=4.372$ Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was $Ed=46.685$ keV Å.

hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
100	2.337	2.336	42.8	81.5
002	2.188	2.186	20.6	52.9
101	2.060	2.060	100	100
102	1.597	1.596	6.4	16.5
110	1.349	1.349	8.4	19.7
103	1.237	1.237	3.5	3.78
200	1.162	1.168	3.0	1.67
112	1.148	1.148	1.4	6.65
201		1.128	a	1.77
004		1.093	b	0.11
202	1.027	1.030	0.69	0.67

^aThe presence of the (331) peak of BeS may have precluded the observation of this peak. See Table I.

^bThe presence of the (420) peak of BeS may have precluded the observation of this peak that is expected to be very weak. See Table I.

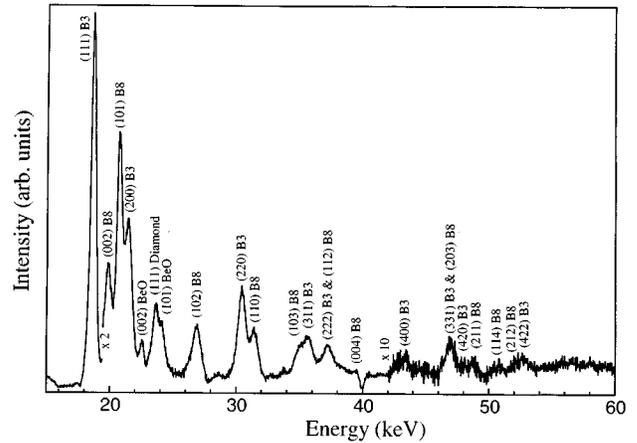


FIG. 4. The x-ray-diffraction pattern at 66.0 GPa for the BeS and BeO mixture. $Ed=46.686$. CESR energy at 5.28 GeV. The BeS has both zinc-blende, $B3$, and NiAs, $B8$, phases present. The only BeO peaks observed are for the wurzite ($B4$) phase.

atom position parameter $Z=0.3786$ given in the literature.²⁶ The agreement with the interplanar spacings is good but the intensity ratios are in poor agreement. We note that there appears to be a preferred orientation that makes the (101) plane, and hence the (202) plane, appear too often, by about a factor of 2. Note that were the number of diffracting (101) planes [and hence (202) planes] to decrease by about a factor of 2, the overall agreement would be much better excepting the (200) peak. It should be noted that the strongest BeO peak is only 11.4% or about $\frac{1}{9}$ as strong as the strongest BeS peak. From the earlier determined Debye-Waller factors for BeO,²⁶ the relative intensity of the (202) peak (for which the effect would be the largest) would be reduced by thermal effects by 14%.

Figure 4 shows the diffraction pattern at 66.0 GPa (the pressure was measured from the EOS of BeS determined in the first experiment; no marker was used so that marker peaks would not interfere; this strategy was nullified by the appearance of BeO as noted earlier). Here we have mixtures of the $B3$ and $B8$ phases²⁷ of BeS as well as peaks from BeO. The indexing of the two structures is shown in Tables III and IV. The d spacings for the zinc-blende phase are in fair agreement but not as good as in Table I because of strain broadening brought about by the uniaxial loading in the diamond-anvil cell. The zinc-blende phase at 66 GPa shows a preferred orientation. If the experimental occurrence of (111) planes was halved, the intensities would be in much better agreement. Because the bulk modulus is over 300 GPa for $P=66$ GPa, the effect of temperature on the intensity is expected to be small.

Table IV summarizes our analysis of the new phase formed, based on our assumption that it is the nickel arsenide, $B8$, phase. The agreement of the d spacing is similar to that for the zinc-blende phase. We note that four peaks expected to be very weak are absent, while the (201) peak could be obscured by the (222) peak of the zinc-blende structure. If the experimental occurrence of (101) planes (only) was doubled, the intensity ratios would be in fair agreement. The c/a ratio of the NiAs varies slowly with pressure approximately according to

TABLE III. List of the observed interplanar spacing and relative intensities I of BeS at 66.0 GPa along with the theoretical corresponding values based on the zinc-blende structure. The fitted lattice parameter $a=4.334$ Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was $Ed=46.685$ keV Å. The fractional volume is $V/V_o=0.708$.

hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
111	2.504	2.506	100	100
200	2.183	2.170	*25.9 ^a	33.9
220	1.534	1.534	17.0	30.9
311	1.310	1.309	7.2	18.7
222	1.255	1.253	1.8 ^b	2.83
400		1.085		1.88
331	0.996	0.996	0.92 ^c	3.00
420	0.971	0.970	*0.16 ^d	1.40

^aThe (100) peak of BeO with $d=2.192$ (see Table V) is likely to make an important contribution. Perhaps one fourth of the 25.9% intensity is due to this BeO peak. See Table V and the discussion associated with it. We did not attempt to deconvolute these and attributed all the intensity to ZB (200).

^bInvolves deconvolution from (112) of the NiAs structure.

^cInvolves deconvolution from (203) of the NiAs structure.

^dInvolves deconvolution from (210) of the NiAs structure.

^eAn asterisk indicates that these planes have some BeO contribution.

$$c/a = 1.61 - 0.0002 P. \quad (2)$$

For BeO at 66 GPa only two peaks were discernible, the 002 and 101 peak. These gave a fractional volume $V/V_o = 0.830$. If the first-order Birch equation (which is equivalent to substituting $B'_o = 4$ in the second-order Birch equation) is used, a *very tentative* bulk modulus $B_o \approx 244$ GPa is obtained for BeO. It is tentative because it should be based on eight to ten peaks, not two. Published values of B_o are shown in Table V.

IV. DISCUSSION

Pearson in 1972 noted that 55 binary phases are known to have the NiAs structure and with but one exception, AuSn, they all contain a transition-metal ion.²⁷ Recent experiments at high pressure have found the additional exceptions: AlAs²⁰ and AlP²¹ among the III-V compounds and BeTe,²⁸ BeSe,²⁸ and BeS among the II-VI compounds. Each of these compounds has a Phillips ionicity $f_i \leq 0.307$.¹⁵ Similar compounds with $f_i \geq 0.307$ tend to form NaCl or β -Sn analogs. BeO ($f_i = 0.602$) is expected to follow this latter pattern.

Van Camp and Van Doren²⁹ have used first-principles self-consistent local-density calculations to compute the properties of BeS. They computed for the ZB phase $B_o = 101.9$ GPa and $B'_o = 3.70$, compared to the presently measured $B_o = 105$ GPa and $B'_o = 3.5$. They calculated that the equilibrium phase transition pressure is 58 GPa. We find 51 ± 8 GPa. The calculated volume of the ZB phase at which the transition began was 0.727 while our experimental volume was 0.724. The calculated volume decrease at the transition was 10.9% while the measured value was 11.0%. Calculations by Muñoz and co-workers³⁰ give for the ZB phase

TABLE IV. List of the observed interplanar spacing and relative intensities I of BeS at 66.0 GPa along with the theoretical corresponding values based on the NiAs structure. The fitted lattice parameters are $a=2.971$ Å and $c=4.711$ Å. The CESR energy was 5.28 GeV and the energy-interplanar spacing product was $Ed = 46.685$ keV Å. The reduced volume is $V/V_o = 0.624$.

hkl	d_{obs} (Å)	d_{calc} (Å)	I_{obs} (%)	I_{calc} (%)
100	2.576	2.573	18.4	9.52
002	2.353	2.354	48.8	16.1
101	2.256	2.256	100	100
102	1.740	1.736	45.4	22.7
110	1.486	1.484	*29.6	15.2
103	1.338	1.339	18.4	8.94
200		1.287		0.43
112	1.257	1.255	*15.6 ^a	5.34
201		1.241	^a	5.76
004		1.177	* ^b	1.30
202		1.128		1.90
104		1.071	* ^c	0.25
203	0.995	0.994	3.1 ^c	2.05
210	0.972	0.972	*0.31 ^d	0.12
211	0.940	0.952	1.1	1.43

^aInvolves deconvolution from the (222) peak of the zinc-blende structure.

^bThere is a diamond dip very near to this peak that precludes measuring this. The dip is caused by the fact that this energy generates a Laue spot of diamond and the absorption that causes this peak decreases the intensity.

^cInvolves deconvolution from the (331) peak of the zinc-blende structure.

^dInvolves deconvolution from the (420) peak of the zinc-blende structure.

^eAn asterisk indicates that these planes can have some BeO contribution.

$B_o = 113.4$, $B'_o = 3.5$, $V_t/V_o = 0.757$, and $P_t = 52.3$ GPa.

It is of interest to compare the bulk moduli of the BeX compounds as shown in Table IV. There is a simple relation

$$B \text{ (GPa)} = 3231/\Omega^{1.018}, \quad (3)$$

where Ω is the atomic volume (Å³). For BeO we used the average value of 227.6 GPa. This is similar to the relation

TABLE V. Bulk moduli and atomic volumes of the BeX compounds.

	Ω (Å ³)	B_o (GPa) _{obs}	Ref.	B_o (GPa) _{calc}	Ref.
BeO	13.485	249 ^a	32	266 ^b	34
		224 ^a	33		
		210	34		
BeS	28.72	105		101.9	31
BeSe	33.89	92.2	29	92.2	32
BeTe	44.31	66.8	29	68.2	3

^aUltrasonic values.

^bThe calculated values are 0 °K, static lattice values while the experimental values are near 300 °K.

given by Zhang and Cohen for III-V compounds.³⁵ If a Born ionic model with a $1/r^n$ repulsion were used with n constant for all the materials, then the exponent would be $1.3\bar{3}$ instead of 1.018. For the III-V ZB compounds, the exponent is 1.16.³⁵

Luo *et al.*²⁸ have noted that based on empirical evidence the NiAs structure appears to be exceptionally stable when $c/a < 1.6\bar{3}$ (the ideal ratio for hcp crystals) while compounds with a higher c/a ratio (FeS, FeSe, MnTe) become unstable at high pressure. (The ideal ratio for the NiAs structure is $1.3\bar{3}$; NiAs, itself, has $c/a = 1.391$.) It would be an interesting problem for theorists to study the stability of the NiAs structure at very high pressures where eventually a transition to eightfold or higher coordination could be expected.

The transition-metal compounds with the NiAs structure are metals. Of the starting BeX compounds (S, Se, Te) BeSe was gray but transparent while BeS and BeTe were opaque because of impurities or color centers. From visual observation at high pressure, there was no evidence that the high-pressure phase had become metallic (they did not appear highly reflective). Further optical and electrical measurements should be made because, if nonmetallic, they would be the first nonmetallic compounds having the NiAs structure.

Luo *et al.* had noted that both BeTe and BeSe transformed when $V_t/V_o = 0.715$ and suggested that BeS and BeO might do the same. However, the transition fractional volume (0.727) was higher for BeS, i.e., it transformed at a lower compression and pressure than expected. They had in the same way estimated that BeO would transform at 139 GPa. We might now expect this to be an upper bound. A

recent *ab initio* study leads to 137 GPa.³⁴ Van Camp and Van Doren³⁴ review earlier calculations. Since the calculations of Van Camp and Van Doren agree well with the experimental transition pressures in BeTe, BeSe, and BeS, we can reasonably expect their calculations for BeO to be correct.

V. CONCLUSIONS

(1) BeS transforms from the ZB structure to the NiAs structure at 59 GPa on unloading with an 11% volume decrease at the transition. The NiAs structure is stable to 96 GPa, the highest pressure studied. On unloading the ZB phase begins to reappear at 43 GPa. The equilibrium transition pressure is 51 ± 8 GPa. The bulk modulus of the ZB phase at zero pressure is 105 ± 2 GPa and its pressure derivative at zero pressure is $B'_o = 3.5 \pm 0.1$.

(2) The fractional volume of BeS at the transition is $V_t/V_o = 0.727$, somewhat higher than found for BeTe and BeSe (0.715), suggesting that the transition in BeO may be somewhat less than the 139 GPa suggested earlier.

(3) The question of whether the NiAs forms of BeS, BeSe, and BeTe remain insulators or not deserves further study.

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- ¹T. Li, H. Luo, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. DiSalvo, Jr., *Phys. Rev. Lett.* **74**, 5232 (1995).
- ²H. Luo, K. Ghandehari, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. DiSalvo, Jr., *Phys. Rev. B* **52**, 7058 (1995).
- ³S. J. Duclos, Y. K. Vohra, A. L. Ruoff, S. Filipek, and B. Baranowski, *Phys. Rev. B* **36**, 7664 (1987).
- ⁴K. Syassen, *Phys. Status Solidi* **91**, 11 (1985).
- ⁵S. Ekbundit, A. Chizmeshya, R. LaViolette, and G. H. Wolf, *J. Phys.: Condens. Matter* **8**, 8251 (1996).
- ⁶T. A. Grzybowski and A. L. Ruoff, *Mater. Res. Soc. Symp. Proc.* **22**, 43 (1984).
- ⁷T. A. Grzybowski and A. L. Ruoff, *Phys. Rev. B* **27**, 6502 (1983).
- ⁸S. T. Weir, Y. K. Vohra, and A. L. Ruoff, *Phys. Rev. B* **33**, 4221 (1986).
- ⁹L. Liu and W. A. Bassett, *J. Geophys. Res.* **77**, 4934 (1972).
- ¹⁰H. K. Zimmer, H. Winzen, and K. Syassen, *Phys. Rev. B* **32**, 4066 (1985).
- ¹¹H. Luo, R. G. Greene, and A. L. Ruoff, *Phys. Rev. B* **49**, 15 341 (1994).
- ¹²Y. Sato and R. Jeanloz, *J. Geophys. Res.* **86**, 11 (1981); **86**, 73 (1981).
- ¹³H. Luo, R. G. Greene, K. Ghandehari, T. Li, and A. L. Ruoff, *Phys. Rev. B* **50**, 16 232 (1994).
- ¹⁴R. Jeanloz, T. Ahrens, H. K. Mao, and P. M. Bell, *Science* **206**, 829 (1979).
- ¹⁵J. C. Phillips, *Bonds and Bands in Semiconductors* (Academic, New York, 1973).
- ¹⁶O. Madelung, *Semiconductors-Basic Data* (Springer-Verlag, New York, 1996).
- ¹⁷A. L. Ruoff and T. Li, *Annu. Rev. Mater. Sci.* **25**, 249 (1995).
- ¹⁸M. I. McMahon and R. J. Nelmes, *J. Phys. Chem. Solids* **56**, 485 (1995).
- ¹⁹M. I. McMahon and R. J. Nelmes, *Phys. Status Solidi* **198**, 389 (1996).
- ²⁰R. G. Greene, H. Luo, T. Li, and A. L. Ruoff, *Phys. Rev. Lett.* **72**, 2045 (1994).
- ²¹R. G. Greene, H. Luo, and A. L. Ruoff, *J. Appl. Phys.* **76**, 7296 (1994).
- ²²J. C. Jamieson, J. Fritz, and M. H. Manghnani, *Adv. Earth Planet. Sci.* **12**, 27 (1980).
- ²³A. L. Ruoff, H. Luo, H. Xia, and Y. K. Vohra, *High Press. Res.* **6**, 183 (1991).
- ²⁴F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ²⁵M. Baublitz, V. Arnold, and A. L. Ruoff, *Rev. Sci. Instrum.* **52**, 1616 (1981).
- ²⁶T. M. Sabine and S. Hogg, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25**, 2254 (1969).
- ²⁷W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys* (Wiley-Interscience, New York, 1972).
- ²⁸H. Luo, K. Ghandehari, R. G. Greene, A. L. Ruoff, S. S. Trail, and F. J. DiSalvo, Jr., *Phys. Rev. B* **52**, 7058 (1995).
- ²⁹P. E. Van Camp and V. E. Van Doren, *Solid State Commun.* **98**, 741 (1996).
- ³⁰A. Muñoz, P. Rodríguez-Hernández, and A. Muijica, *Phys. Status*

- Solidi **198**, 439 (1996).
- ³¹G. G. Bentle, J. Am. Ceram. Soc. **49**, 125 (1966).
- ³²C. F. Cline, H. L. Dunegan, and G. W. Henderson, J. Appl. Phys. **38**, 1944 (1967).
- ³³R. M. Hazen and L. W. Finger, J. Appl. Phys. **59**, 3728 (1986).
- ³⁴P. E. Van Camp and V. E. Van Doren, J. Phys.: Condens. Matter **8**, 3385 (1996).
- ³⁵S. B. Zhang and M. L. Cohen, Phys. Rev. B **35**, 7604 (1987).