Band structures of CsCl-structured BaS and CaSe at high pressure: Implications for metallization pressures of the alkaline earth chalcogenides

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The indirect energy gaps of CsCl-structured BaS and CaSe are measured at high pressures using absorption spectroscopy to pressures of 41 and 53 GPa, respectively. Band-structure calculations using density-functional theory and quasiparticle corrections are also conducted on BaS and CaSe as a function of pressure. The measured indirect gaps of BaS and CaSe shift linearly with pressure with a slope, (dE_{gap}/dP), of $-1.8(2) \times 10^{-2}$ and $-1.5(3) \times 10^{-2}$ eV/GPa, respectively. These values are in reasonable agreement with the theoretical results of -2.2×10^{-2} eV/GPa for BaS and -2.3×10^{-2} eV/GPa for CaSe. Our calculations indicate that the energy gap in both compounds is indirect with the valence-band maxima at **M** and the conduction-band minima at **Γ**. Based on a simple linear extrapolation of our data, we estimate the metallization pressures of CsCl-structured BaS and CaSe to be above 113 and 125 GPa, respectively. Our estimates of metallization pressures are compared with those of other alkaline earth monochalcogenides to determine the degree to which changes in the electronic structures of these compounds under pressure can be described using systematic trends based on ionic radii. [S0163-1829(98)03839-9]

I. INTRODUCTION

The properties of the heavy alkaline earth chalcogenides are a subject of considerable theoretical and experimental interest. These closed shell ionic systems share similar band structures and, in turn, have similar physical properties. With the exception of BaO,[1] all of the Ca, Sr, and Ba chalcogenides transform from the NaCl to CsCl structure under compression. The metallization of these compounds at high pressure remains a subject of study: BaTe, SrTe, and BaSe have been observed to metallize near 27, 55, and 52 GPa, respectively.[2,3] Both theoretical and experimental estimates of the metallization pressures of other alkaline earth chalcogenides have been made.[1–9] In order to understand the band structure of these compounds and their rate of change with pressure, we examine CaSe and BaS under pressure from both experimental and theoretical viewpoints.

BaS and CaSe convert to the CsCl structure from the lower-pressure NaCl structure at pressures near 7 and 39 GPa, respectively.[10,11] The band structures of both NaCl and CsCl-structured Ca, Sr, and Ba chalcogenides have upper valence-band p states and d-like conduction bands. Most of the compounds examined to date by experimental methods have indirect gaps produced by $\mathbf{\Gamma} \rightarrow \mathbf{X}$ transitions in the rocksalt phase and indirect gaps from $\mathbf{M} \rightarrow \mathbf{\Gamma}$ in the CsCl structure.[4,7–9,12–14] However, ambient pressure theoretical calculations of the oxides,[12,15] SrS, CaS,[15] and a previous theoretical calculation of CaSe (Ref. 13) result in band structures of the NaCl-structured phases that have direct gaps.[12,13,15]

Our principal goal is to determine the shift with pressure of the electronic structures of the CsCl-structured phases of BaS and CaSe. In particular, the shift of the energy gap, (dE_{gap}/dP), is useful for estimating the pressure at which metallization might occur. Furthermore, the energy gap between the valence and conduction bands of these CsCl-structured phases can be identified as direct or indirect by measuring the absorption spectrum of pressurized samples. We present measurements of energy gaps of the CsCl-structured BaS and CaSe to 41 and 53 GPa, respectively, and new theoretical band-structure calculations on these two compounds. These are the first optical studies of CsCl-structured CaSe; a possible metallization pressure of BaS of 80 GPa has been previously proposed based on unpublished optical data.[3] The experimentally determined shifts with pressure of band gaps provide a particularly rigorous test of theoretical calculations of semiconductor band structures: in both CaSe and BaS, the band calculations are demonstrated to be in agreement with the experimental data. Finally, we utilize our results to examine trends of metallization pressures among the alkaline earth chalcogenides.

II. EXPERIMENTS

Absorption spectra of the indirect gaps of CsCl-structured BaS and CaSe were measured using a modified Mao-Bell diamond-anvil cell.[16] The samples used were powders of 99.5% purity from Alfa-Ventron, Inc. The apparatus used for measuring the optical spectra is identical to that described in a previous study.[17] A preindented inconel gasket with an approximately 200-μm-diam hole was used to contain samples between type-I diamonds with 350-μm-diam culets. The powdered samples were loaded into the hole with multiple grains of ruby powder placed on top of the samples. No

pressure medium was used with either material to avoid potential decomposition of these hydroscopic salts. For BaS, which underwent a rapid change in electronic structure with pressure, an aperture of indium foil was placed over the gasket to ensure that the absorption measurements sampled only the highest pressure center of the sample. The aperture was approximately 100 μm in diameter and remained about this size over our entire pressure range. Pressure measurements were made using the well-known ruby fluorescence technique,[18] with pressure monitored at several points in the sample to characterize pressure gradients; because of the relatively large band gaps of these materials, absorptions associated with the ruby pressure calibrant have no effect on our results. The thickness of samples used in these runs was approximately 6–8 μm thick.

Under transmitted light, BaS changes in color with pressure. From ambient pressure to roughly 6 GPa, BaS appears light gray, probably due to grain boundary scattering. At 7 GPa, during the NaCl- to CsCl-structure transition,[1,10] the sample becomes bright yellow. With a slight increase in pressure, the yellow color changes to gold. By 9 GPa, the sample visually appears to be a mosaic of brown and orange, probably due to variations in sample thickness, and remains orange to about 12 GPa, where it becomes red. The red deepens with increasing pressure until the sample becomes completely opaque at roughly 20 GPa.

CaSe undergoes similar changes in appearance under transmitted light. The powder is brownish at ambient pressure and remains so to 14 GPa, where dark streaks and gold spots develop. At 40 GPa, during the NaCl- to CsCl-structure transition,[11] the sample becomes visually opaque with a few orange spots. The orange spots darken to brown and red by approximately 45 GPa, and the sample becomes completely opaque by 47 GPa. This description is in contrast with an observation of transmitted light reported at 50 GPa in CaSe.[11] The dark streaks appearing at high pressures are thought to be caused by defects. Similar defect-induced heterogeneity in sample color has also been observed in pressurized CdS,[17] ZnS,[19] CuBr, CuCl, and HI under pressure.[20,21]

III. RESULTS

Optical measurements provide a straightforward way to determine the band gaps of semiconductors under pressure:[22] unlike electrical conductivity measurements, such measurements are not aliased by complex scattering effects at low temperature.[23] For substances with an indirect energy gap that is optically allowed, the absorption spectrum will show a quadratic dependence on energy near the band edge; departures from such quadratic behavior are often associated with defect absorption. Ignoring defects, the absorption coefficient, α, of such a system is[22]

$$\alpha = \mathrm{const} \times (E - E_{\mathrm{gap}} - E_{\mathrm{phonon}})^2, \qquad (1)$$

where E is the energy of light and E_{phonon} is the energy of the phonon that allows the shift in k space associated with the indirect transition. We neglect the E_{phonon} term because it is likely to be a maximum of approximately 5% of our measured gaps.
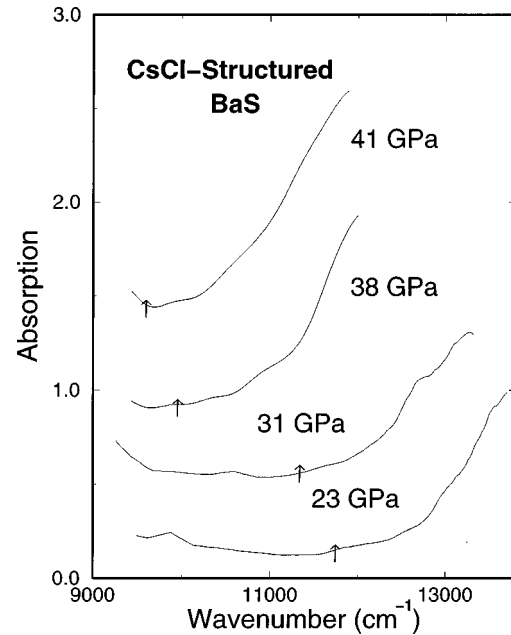

FIG. 1. BaS absorption spectra at high pressure; absolute absorption values are displaced along the y axis for display purposes. Arrows show location of gap as derived from the quadratic extrapolation of the high-energy absorption structure.

Representative absorption spectra of BaS are shown in Fig. 1. For this material, the observed absorption spectra edges were preceded by lower-energy linear band tails in all runs: these may be produced by scattering effects. The square root of absorption shifts systematically to lower energy with compression (Fig. 2). The parallelism of the lines in Fig. 2 suggests that little broadening of either the conduction band minima or broadening of the valence-band maximum occurs under pressure. The spectra were analyzed by fitting parabolas to the high-frequency end of the spectra, where band tails have a minimal contribution. The variation in energy of the band gap of BaS at high pressure is shown in Fig. 3. The band gap appears to shift linearly over this pressure range, with a slope of $-1.8(2) \times 10^{-2}$ eV/GPa. This is in reasonable accord with our calculated theoretical value of -2.2×10^{-2} eV/GPa, described below.

CaSe absorption spectra are shown in Fig. 4. In this material, some absorption was observed near 0.37 eV. Similar structure has been observed near this energy in BaTe and CdSe under compression:[2,17] this phenomenon is not well understood, but may be due to defects induced by either
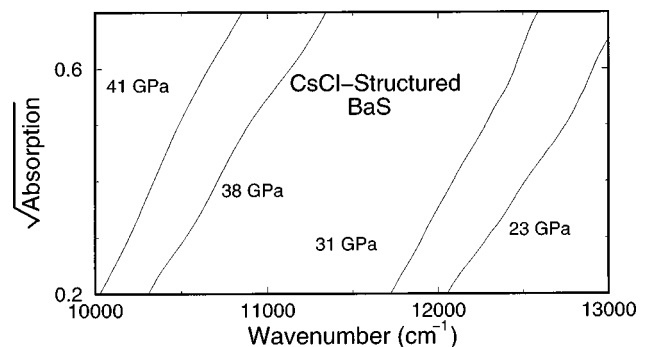

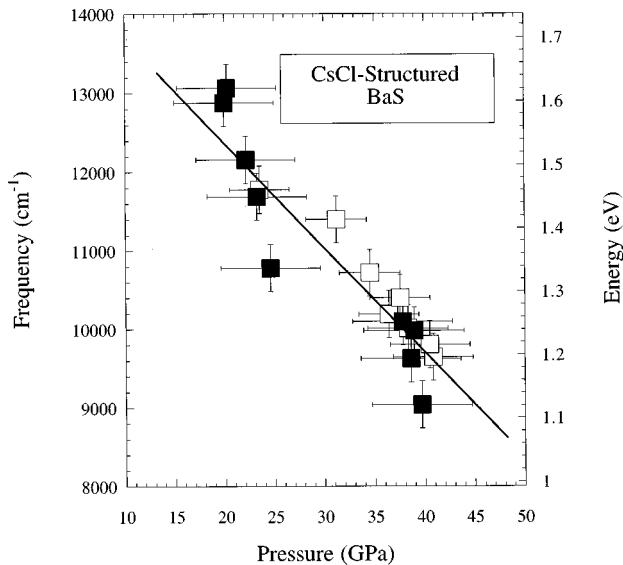FIG. 2. Square root of BaS absorption for different pressures.

FIG. 3. Dependence of BaS energy gap on pressure. Closed squares represent values measured upon compression, while open squares represent values measured upon decompression.

pressure gradients, phase transitions, or impurities such as hydrocarbon contamination from the gasket. As with BaS, the dependences of the square root of absorption on energy for CaSe are parallel and show a systematic decrease in energy with compression (Fig. 5). The pressure dependence of the band gap of CaSe is also linear with pressure to within the accuracy of our measurements, and the slope of the energy-gap shift is determined to be $-1.5(3) \times 10^{-2}$ eV/GPa (Fig. 6), in reasonable accord with our calculated theoretical value of -2.3×10^{-2} eV/GPa.

Clearly, neither BaS nor CaSe metallize over the pressure range of our data; they remain indirect-gap semiconductors
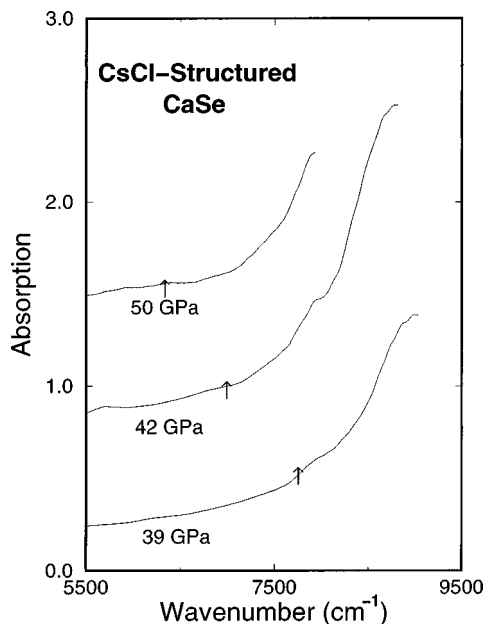

FIG. 4. CaSe absorption spectra under pressure. Spectra are displaced in absorption for clarity. Arrows show location of gap as derived from the quadratic extrapolation of the high-energy absorption structure.
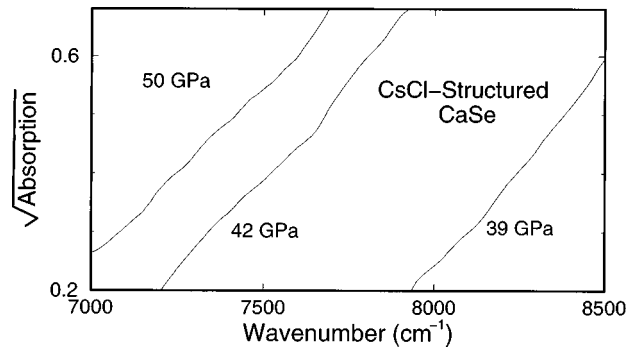

FIG. 5. Square root of the CaSe absorption spectra at different pressures.

throughout our range of volumetric compaction. If we assume that the experimental pressure shifts of the gaps continue to be linear, we predict that CsCl-structured BaS and CaSe will metallize near 113 and 125 GPa, respectively.

In order to further understand the behavior of these compounds, we conducted theoretical electronic band-structure calculations for both these CsCl-structured compounds using density-functional theory and norm-conserving pseudo-potentials.[24] The exchange-correlation energy of the electrons is treated in the local-density approximation.[25,26] We used Hamann, Schlüter, and Chiang pseudopotentials[27] for the Se and Ba atoms and Troullier and Martins pseudopotentials[28] for the Ca and S atoms. In all cases, we constructed pseudopotentials for the s, p, and d valence orbitals. The electron charge density is represented by a plane-wave basis[29] where we use an energy cutoff of 60 and 90 Ry for BaS and CaSe, respectively. The k-point sampling was done by the Monkhorst-Pack scheme[30] where we employed 10 irreducible k points for the total-energy calculations.

It is well known that the energy gap of a semiconductor is systematically underestimated by density-functional theory. To overcome this problem, quasiparticle (QP) corrections were implemented.[31] The QP corrections are calculated within the GW approximation for the electronic self-energy
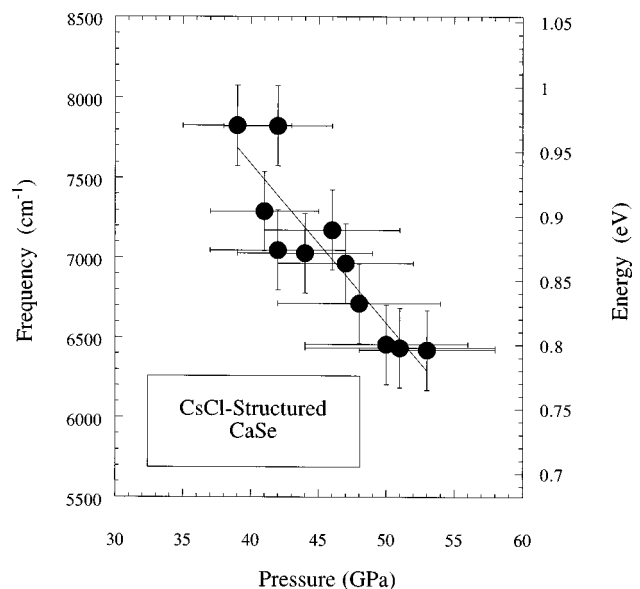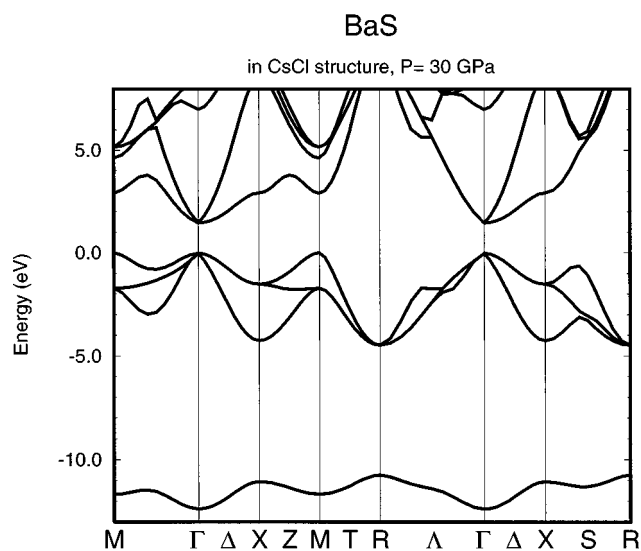

FIG. 6. Dependence of CaSe energy gap on pressure.

BaS

in CsCl structure, P= 30 GPa

FIG. 7. Calculated band structure for BaS at 30 GPa. The gap is indirect from $\mathbf{M} \rightarrow \boldsymbol{\Gamma}$. The zero of energy is defined to be the maximum of the valence band. The conduction bands have been shifted to the calculated *GW* energies.

(for details, see Ref. 32). The main effect of the QP corrections is a nearly rigid shift of all conduction bands to higher energies. The resulting band structures of the BaS and CaSe compounds in the CsCl structure are shown in Figs. 7 and 8, respectively. The calculated QP gaps are in very good agreement with the experimental data. For instance, the calculated gap of CsCl-structured BaS at 30 GPa is found to be 1.46 eV, which is in close accord with the experimental value of 1.35(5) eV. For CaSe, the theoretical value of the energy gap is 0.65 eV at 50 GPa, whereas the experimental value is 0.81(5) eV. The differences between the experimental and theoretical values are within the accuracy of the theoretical method.
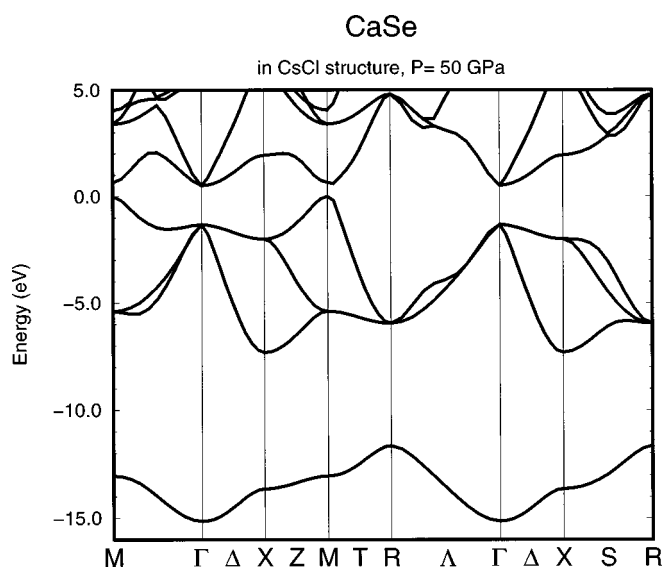
CaSe

in CsCl structure, P= 50 GPa

FIG. 8. Calculated band structure for CaSe at 50 GPa, with an indirect gap from $\mathbf{M} \rightarrow \boldsymbol{\Gamma}$. The zero of energy is defined to be the maximum of the valence band. The conduction bands have been shifted to the calculated *GW* energies.

We also considered the pressure dependence of the energy gap by performing calculations for several pressures. Between 9 and 50 GPa, we found that the energy gap of BaS is from the $\mathbf{M}$ point of the valence complex to the $\boldsymbol{\Gamma}$ point of the conduction band. A linear relationship between the energy gap and the pressure is obtained for this pressure range with a slope of -2.2×10^{-2} eV/GPa, which is in good agreement with previous calculations[8] and the present experimental values. For pressures above 50 GPa, the energy gap becomes direct at $\boldsymbol{\Gamma}$ with a slope of -2.5×10^{-2} eV/GPa. The dipole matrix element of this direct transition has been evaluated and determined to be forbidden. This particular type of transition should yield absorption spectra with an edge that rises as $(E - E_{\mathrm{gap}})^{(3/2)}$. The pressure at which the gap becomes direct is difficult to evaluate precisely and could have an error of up to 10 GPa. We did not observe any shift of the character of the energy gap in the present experiment, which suggests that any shift to a structure with a direct transition must occur at pressures above 41 GPa. Such a change in the nature of the gap might explain why metallization was inferred to occur in this compound at 80 GPa (Ref. 3) instead of 113 GPa, as derived from the pressure dependence of the indirect gap in the current experiment. Nevertheless, our results indicate that differing *k*-space transitions could generate the lowest optical gap in heavy alkaline earth chalcogenides: The $\mathbf{M}$ and $\boldsymbol{\Gamma}$ points appear to have the highest valence-band states, as well as the lowest conduction-band states.

In the case of CaSe, the gap is found to be indirect with a $\mathbf{M} \rightarrow \boldsymbol{\Gamma}$ transition for all pressures considered. According to the band structure (Fig. 8), a shift to a direct transition at the $\mathbf{M}$ point might be possible; however, such a shift is predicted to occur at a pressure lower than 30 GPa, where the CsCl structure is energetically unfavorable with respect to the rocksalt structure. The calculated pressure dependence of the indirect energy gap is -2.3×10^{-2} eV/GPa, in reasonable agreement with the present experimental results. In CaSe, the bottom of the conduction band has similar energies at the $\boldsymbol{\Gamma}$ and $\mathbf{M}$ points, while in BaS it is the top of the valence band that has similar energies at these points. Therefore, in spite of their identical structures and similar electronic properties, important differences in band structure exist between the two compounds.

The pressure dependences of the energy gap for these two compounds are significantly larger than those of NaCl-structured IIB-VI compounds such as CdS and CdSe.[17] This behavior can be explained by considering the decomposition of the wave functions that contribute to the gap transition. Our theoretical analysis shows that the maximum of the valence band at $\mathbf{M}$ for the BaS compound is essentially composed of sulfur *p* orbitals and the wave functions of the CaSe compound are composed of 95% Se *p* orbitals and 5% Ca *p* orbitals. In contrast, the minimum of the conduction band of BaS at $\boldsymbol{\Gamma}$ is 82% Ba *d* orbitals and 18% S *d*, while in CaSe it is 76% Ca *d* and 24% Se *d* orbitals. The kinetic energy of all the states is increased when the crystal is compressed, leading to an upward energy shift of all bands with respect to the vacuum level. Since the wave functions of the lowest conduction band consist of strongly localized *d* orbitals, they are much less affected by the lattice contraction and undergo a much smaller energy shift than the more delocalized highest

valence states. As a result, the energy gap is reduced rapidly under compression. In the NaCl-structured IIB-VI semiconductors such as CdS and CdSe under pressure, the eigenfunctions participating in the energy gap do not contain as much d character. Hence, all eigenvalues move up at roughly the same rate with respect to the vacuum level as pressure is applied and a substantially smaller pressure shift is observed. This larger pressure dependence of the IIA-VI compounds relative to the IIB-VI compounds is therefore attributed to the atomic levels of the IIA elements, in which their d states lie closest to the occupied levels.

In an effort to develop a systematic understanding of trends of metallization pressures in the alkaline earth monochalcogenides, we utilized and modified the previous quasiempirical trend originally proposed by Syassen,[33–35] and introduce an alternative parameter, $\log_{10}(R_M^{-1})$, as a means of viewing such trends in a more intuitive manner. The NaCl- to CsCl-structure transition pressures of these monochalcogenides were shown to follow an exponential trend with respect to the empirical coordinate:[34,35]

$$R_M^{-1} = (r_c^{-2} + r_a^{-2})^{1/2}, \qquad (2)$$

where r_c and r_a are the ambient pressure cation and anion radii, respectively. A general correlation has also been noted between this coordinate and metallization pressure.[34,35] We update these trends and evaluate the degree to which correlations between R_M^{-1} and transition/metallization pressures can be applied to a wider series of compounds. Instead of using R_M^{-1}, we correlate the $\log_{10}$ of pressure with $\log_{10}(R_M^{-1})$. The correlation between $\log_{10}(R_M^{-1})$ and the log of pressure can be derived by assuming the lattice energy of the alkaline earth chalcogenide compounds is proportional to an inverse power-law potential, and utilizing the thermodynamic relation relating pressure to the derivative of energy with respect to volume. The pressure is thus predicted to be proportional to a power of the interatomic spacing R. As the alkaline earth chalcogenides are isostructural and isoelectronic, this correlation implicitly assumes that the transition pressures depend only upon the spacing between the ions, or the mean radius R_M.

Figure 9(a) shows the correlation of R_M^{-1} with phase transition and metallization pressures, updated with recent experimental values,[2,3] as well as theoretical estimates of metallization pressures for compounds where experimentally derived estimates were unavailable.[1,4,5] Figure 9(b) shows the corresponding correlation with $\log_{10}(R_M^{-1})$; Figs. 9(a) and 9(b) have comparably good correlations. The estimated pressures for band overlap, which were derived from theoretical results, are inferred to have error bars which correspond to the 40–50 % underestimation of the energy gap due to the local-density approximation (Fig. 9):[36,37] this assumption likely provides a highly conservative estimate of the errors on these values. We calculate an approximate pressure dependence of the gap of SrS from experimental observations.[34] SrS appears yellow in transmitted light at 18 GPa and red at 35 GPa.[34] By analogy with BaS, and presuming that this color change reflects the pressure shift of the intrinsic gap,[38] the pressure dependence of the gap of SrS is estimated as $-2(1) \times 10^{-2}$ eV/GPa, a value in accord with our measured pressure dependences of BaS and CaSe. Utilizing a gap for SrS at 18 GPa of 2.1 eV, and assuming that
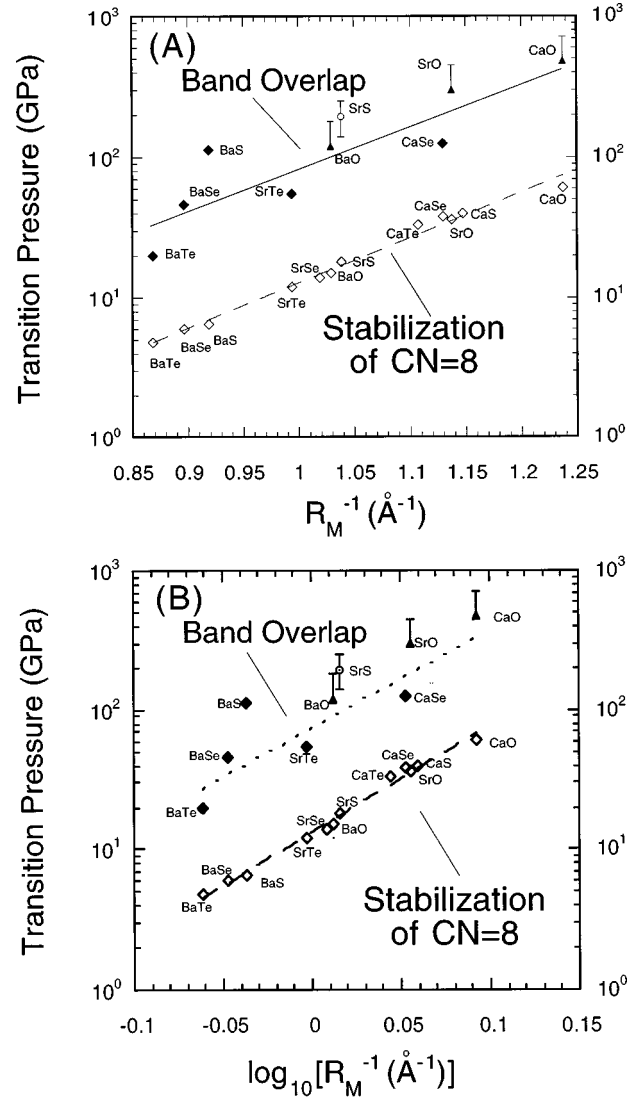

FIG. 9. (a) Dependence of metallization and phase transition pressures on R_M^{-1}. The pressures at which a transition to phases with a coordination number of 8 occurs in the alkaline earth chalcogenides are shown by the open diamonds: for all compounds except BaO, these correspond to the NaCl→CsCl transition. The closed diamonds represent experimentally inferred values of metallization. Closed triangles show results of theoretical calculations, and are plotted along with a 50% upper error bar to account for the underestimation of the energy gap that is characteristic of the local-density approximation technique (Refs. 36 and 37). The open circle for SrS is an experimentally based estimate of metallization pressure (see text). Values of band overlap for CaO,[4] SrO,[1] and BaO (Ref. 5) are theoretical, while metallization values for SrTe, BaTe,[6] and BaSe (Ref. 3) are experimental. The B1-B2 phase transition pressures of CaO are from Ref. 43; CaS, CaSe, and CaTe from Ref. 11; SrSe from Ref. 42; SrS from Ref. 34; SrO from Ref. 44; SrTe and BaTe from Ref. 2; BaO from Ref. 1; BaS from Ref. 10; and BaSe from Ref. 3. (b) The dependence of band overlap and phase transition pressures on $\log_{10}(R_M^{-1})$.

this material has a smaller pressure dependence of the gap than BaS, we estimate a metallization pressure for SrS of 190 ± 50 GPa. The Ba, Sr, and Ca chalcogenide series lie close to one another in the parameter R_M^{-1}, with the oxides removed from these clusters due to the relatively small an-
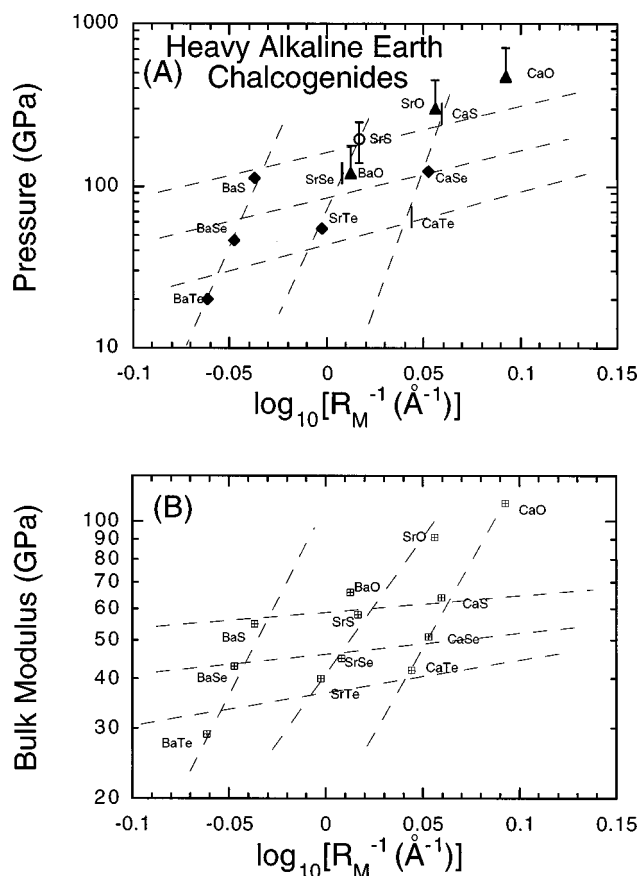
FIG. 10. (a) The dependence of metallization pressures on the logarithm of reciprocal mean ionic radius. Symbols are identical to Fig. 9. The compositional trends for constant cation and anion makeup are shown with dashed lines. The vertical lines represent estimates of the metallization pressures (see text). (b) The bulk moduli of NaCl-structured alkaline earth metal chalcogenides and oxides versus logarithm of reciprocal mean ionic radius. Bulk moduli values for CaO are from Ref. 40, for CaS, CaSe, and CaTe from Ref. 11, for SrO and SrS from Ref. 34, for SrSe from Ref. 42, for SrTe from Ref. 6, for BaO and BaS from Ref. 1, for BaSe from Ref. 45, and for BaTe from Ref. 46.

ionic radius of oxygen [Fig. 9(a)]. The metallization pressures of the Ba chalcogenides rise exponentially as progressively lighter chalcogenides are incorporated into the CsCl structure. Simple systematics demonstrate that the heavier members of an isoelectronic series tend to metallize at lower pressures.[17,39] For example, CsCl-structured BaSe and BaTe metallize at 52 (Ref. 3) and 27 GPa,[2] respectively. In agreement with this trend, our estimate for the metallization pressure of BaS is in excess of 110 GPa.

If similar slopes on Figs. 9(a) and 9(b) are assumed to exist for the Ca and Sr chalcogenides as for the Ba series, semi-quantitative predictions of metallization pressures can be made for CaS, CaTe, and SrSe. These are plotted in Figure 10(a) and shown with vertical lines. The bulk moduli of the NaCl-structured phases follow similar trends in $\log_{10}(R_M^{-1})$ indicating the applicability of inverse power-law potentials in approximately describing the physical properties of the IIA-VI compounds [Fig. 10(b)]. It is likely that pressures in excess of 200 GPa are required to metallize CaS; none of the oxides appear likely to metallize at pressures below 200 GPa, as well.[1,40] This is in accord with the con-

tinued transparency to visible light of BaO and CaO to pressures in excess of 100 GPa.[1,40] If the oxides lie on the trend defined by the other chalcogenides, previous theoretical estimates of oxide metallization pressures could be strongly underestimated.[1,4,5] The exponential fit for the pressures of the structural transition from the NaCl to the CsCl structure from Fig. 9(a) is

$$\log_{10}(P_t) = 3.2(R_M^{-1} - 0.66), \tag{3}$$

where P_t is the pressure of the structural transition in GPa. This slope is slightly less than Syassen's calculated fit[34] of 3.5, based upon transition pressures of nine compounds. For comparison, the fit equation for the trend of the pressures of metallization with mean inverse ionic radius is

$$\log_{10}(P_m) = 3.0(R_M^{-1} - 0.35), \tag{4}$$

where P_m is the pressure of metallization in GPa. It is clear that such a fit averages through the more rapidly increasing respective trends of the metallization pressures of the individual Ba-, Sr-, and Ca-chalcogenide series, but rather closely mirrors the general trend of the alkaline earth-Te and -Se series. In this sense, the average trend for metallization [Eq. (4)] closely follows that of the apparent trends of the metallization pressures for compounds with the same anions. Similarly, the fits for Fig. 9(b) are

$$\log_{10}(P_t) = 7.7[\log_{10}(R_M^{-1}) + 0.15] \tag{5}$$

and

$$\log_{10}(P_M) = 8[\log_{10}(R_M^{-1}) + 0.23]. \tag{6}$$

From Eq. (5), it can be seen that the hypothesized average power-law potential is proportional to $R^{-4.7}$, where pressure is again the derivative of the internal energy with respect to volume. Though the metallization pressures for these compounds follow a similar trend to that of the phase transition, [Eq. (6) and Figs. 9(a) and 9(b)], it is not surprising that there is much more scatter in the metallization trend. Not only is the quality of the constraints on metallization pressure poorer than on the transition pressure, but the pressure at which a compound metallizes depends heavily on both its band structure and bulk modulus. Figure 10(a) illustrates this difference in trends of metallization pressure between isocationic and isoanionic series. Clearly, retaining the same anion results in a considerably smaller increase in metallization pressure as cation size (and electron density) is reduced than does retaining the same cation and changing the anion. This difference in trends is likely a consequence of a relatively larger change in energy of the valence-band anion p states as one moves to lighter chalcogenides, as compared to a smaller change in energy of the conduction-band d states of the cations as one moves to lighter alkaline earths. In short, the atomic levels of the different elements appear to play a dominant role in determining the detailed trends of metallization in this series: the anionic (and relatively delocalized) p states apparently change more in energy within their isoelectronic series than do the more localized cationic d states, as reflected in Fig. 10(a). The importance of the differing behavior of the valence (anion-derived) and conduction (cation-derived) states of the alkaline earth chalcogenides for not only metallization, but for other physical manifestations of interionic interactions such as bulk modulus, is shown in Fig. 10(b). This
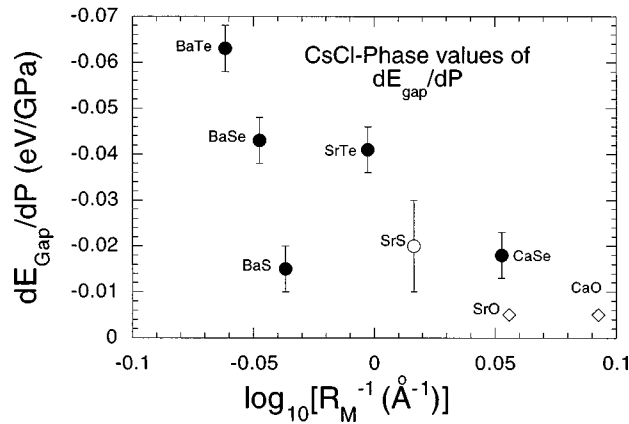
FIG. 11. Pressure dependences of the band gaps of CsCl-structured IIA-VI compounds. The experimentally determined values for SrTe and BaTe (Ref. 2) and BaSe (Ref. 3) are shown along with our present measurements (dark circles). The theoretical pressure dependences for SrO and CaO (Ref. 9) are shown with open diamonds. The estimated dE_{gap}/dP for SrS is shown with an open circle (see text). We present gap shifts rather than deformation potentials for these materials because the bulk moduli for the CsCl-structured phases of several of these materials are ill constrained.

trend indicates the applicability of inverse power-law potentials in providing a gross description of the physical properties of the IIA-VI compounds. Although the bulk moduli values of Fig. 10(b) are for NaCl-structured polymorphs, we expect that similar trends will be present for the CsCl-structured phases: the available elastic data on the high-pressure phases are, however, too limited to assess whether this is the case.

A direct comparison of Figs. 10(a) and 10(b) shows increasing metallization pressure values for increasing respective bulk moduli. The bulk modulus of BaO is observed to deviate below the outlined trends in Fig. 10(a). This low bulk modulus of BaO is accompanied by a phase transition to the NiAs structure at roughly 10 GPa,[1] while all other alkaline earth chalcogenides undergo a transition to the CsCl structure. As with metallization pressure, the bulk moduli are smaller for the heavier compounds and the identity of the anion can be seen to be the primary determinant influencing the bulk moduli of these materials. Similar trends have been observed in other semiconducting compounds such as the IA-VII and IIB-VI series.[17,41]

Measured and calculated values of dE_{gap}/dP for the members of the alkaline chalcogenides are shown in Fig. 11. Clearly, the heavier members of an isoelectronic series have relatively larger pressure dependences of the gap, and correspondingly lower metallization pressures. The underlying physical reasons for such a trend are likely produced by the coupled role of the larger pressure shifts for the more delocalized p states of the heavier chalcogenides and the smaller bulk moduli associated with increasing ionic radii.

IV. CONCLUSIONS

The pressure coefficient, dE_{gap}/dp, for CsCl-structured CaSe was determined to be $-1.5(3) \times 10^{-2}$ eV/GPa, while that of BaS is $-1.8(2) \times 10^{-2}$ eV/GPa. Each of these values are in reasonable agreement with theoretical predictions of -2.3×10^{-2} eV/GPa for CaSe and -2.2×10^{-2} eV/GPa for BaS. Both CaSe and BaS continue to have indirect gaps to pressures of 53 and 41 GPa, respectively. BaS is theoretically predicted to ultimately become a direct-gap semiconductor with a transition at the Γ point for pressures above about 50 GPa. From the continuous change in gap energies, both compounds appear to have gaps corresponding to $\mathbf{M} \rightarrow \Gamma$ transitions throughout the pressure ranges of the experiments, with no fundamental change in band structures observed. From the pressure shifts of the gap energies, we predict that BaS will metallize above 113 GPa, while CaSe will metallize above 125 GPa.

These results are both in accord with, and expand on, previous empirical trends of phase transition and metallization pressure with R_M^{-1}.[34,35] We also utilize trends of transition and metallization pressure with $\log_{10}(R_M^{-1})$ as a means of producing quasiempirical predictive trends of transitions of the heavy alkaline earth monochalcogenides. This dependence is based on the straightforward assumption that lattice energy of such compounds follows a simple inverse power law with volume, or mean radius. Such a relationship yields an averaged power law for the alkaline earth chalcogenides of order $R_M^{-4.7}$. The heavy alkaline earth chalcogenides share grossly similar band structures and, in turn, have structural transformations and band overlap pressures that scale exponentially with the logarithm of the inverse root mean square of their ionic radii, $\log_{10}(R_M^{-1})$. A systematic decrease in the absolute value of the pressure dependence of the gap for progressively lighter alkaline earth chalcogenides is documented: this trend plausibly reflects the increased localization (and resultant pressure insensitivity) of the electronic states of the lighter chalcogenide compounds.

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[1] S. T. Weir, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **33**, 4221 (1985).

[2] K. Syassen, N. E. Christensen, H. Winzen, K. Fischer, and J. Evers, Phys. Rev. B **35**, 4052 (1987).

[3] S. T. Weir, Y. K. Vohra, and A. L. Ruoff, Phys. Rev. B **35**, 874 (1987).

[4] M. S. T. Bukowinski and J. Hauser, Geophys. Res. Lett. **7**, 689 (1980).

[5] J. Hama and M. Watanabe, Phys. Lett. A **115**, 287 (1986).

[6] H. G. Zimmer, H. Winzen, and K. Syassen, Phys. Rev. B **32**, 4066 (1985).

[7] G. Kalpana, B. Palanivel, and M. Rajagopalan, Phys. Rev. B **50**, 12 318 (1994).

[8] A. E. Carlsson and J. W. Wilkins, Phys. Rev. B **29**, 5836 (1984).

[9] G. Kalpana, B. Palanivel, and M. Rajagopalan, Phys. Rev. B **52**, 4 (1995).

[10] S. Yamaoka, O. Shimomura, and O. Fukunaga, Solid State Commun. **33**, 87 (1980).

[11] H. Luo, R. G. Greene, K. Ghandehari, T. Ling, and A. L. Ruoff, Phys. Rev. B **50**, 16 232 (1994).

[12] V. S. Stepanyuk, A. Szasz, A. A. Katsnelson, A. A. Grigorenko, and O. V. Farberovich, Phys. Status Solidi B **171**, K23 (1992).

[13] R. Pandey, P. Lepak, and J. E. Jaffe, Phys. Rev. B **46**, 4976 (1992).

[14] M. J. Mehl, R. E. Cohen, and H. Krakauer, J. Geophys. Res. **43**, 8009 (1988).

[15] R. Pandey, J. E. Jaffe, and A. B. Kunz, Phys. Rev. B **43**, 9228 (1991).

[16] Q. Williams and R. Jeanloz, *Molten Salt Techniques*, edited by R. J. Gale and D. G. Lovering (Plenum, New York, 1991), Vol. 4, p. 193.

[17] P. Cervantes, Q. Williams, M. Côté, O. Zakharov, and M. L. Cohen, Phys. Rev. B **54**, 17 585 (1996).

[18] G. J. Piermarini and S. Block, Rev. Sci. Instrum. **46**, 973 (1975).

[19] S. Ves, U. Schwarz, N. E. Christensen, K. Syassen, and M. Cardona, Phys. Rev. B **42**, 9113 (1990).

[20] J. van Straaten and I. F. Silvera, Phys. Rev. B **36**, 9253 (1987).

[21] D. G. Ves, M. Cardona, and H. Overhof, Phys. Rev. B **24**, 3073 (1981).

[22] J. I. Pankove, *Optical Processes in Semiconductors* (Prentice Hall, New Jersey, 1971).

[23] W. Paul and D. M. Warschauer, *Solids Under Pressure* (McGraw-Hill, New York, 1963).

[24] M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[25] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[26] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[27] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[28] J. L. Martins, N. Troullier, and S.-H. Wei, Phys. Rev. B **43**, 2213 (1991).

[29] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[30] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[31] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[32] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **75**, 3489 (1995).

[33] S. Ekbundit, A. Chizmeshya, R. LaViolette, and G. H. Wolf, J. Phys.: Condens. Matter **8**, 8251 (1996).

[34] K. Syassen, Phys. Status Solidi A **91**, 11 (1985).

[35] K. Syassen, Physica B **139-140**, 277 (1986).

[36] X. Zhu, S. Fahy, and S. G. Louie, Phys. Rev. B **39**, 7840 (1989).

[37] X. Zhu, S. Fahy, and S. G. Louie, Phys. Rev. B **40**, 5821 (1989).

[38] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids **5**, 328 (1958).

[39] A. Jayaraman, W. Klement, Jr., and G. C. Kennedy, Phys. Rev. **130**, 2277 (1963).

[40] P. Richet, H. Mao, and P. M. Bell, J. Geophys. Res. **93**, 15 279 (1988).

[41] K. Asaumi, Y. Kondo, T. Mori, and T. Suzuki, in *Solid State Physics Under Pressure*, edited by S. Minomura (Terra Scientific, Tokyo, 1985), pp. 63–68.

[42] H. Luo, R. G. Greene, and A. L. Ruoff, Phys. Rev. B **49**, 15 341 (1994).

[43] R. Jeanloz, T. J. Ahrens, H. K. Mao, and P. M. Bell, Science **206**, 829 (1979).

[44] Y. Sato and R. Jeanloz, J. Geophys. Res. **86**, 11 773 (1983).

[45] T. A. Grzybowski and A. L. Ruoff, Phys. Rev. B **27**, 6502 (1983).

[46] A. L. Ruoff and T. A. Grzybowski, in *Solid State Physics Under Pressure* (Ref. 41), pp. 69–74.