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Pressure-induced phase transformations in the $\text{Ba}_8\text{Si}_{46}$ clathrate

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The nature of isostructural transformations of a type-I $\text{Ba}_8\text{Si}_{46}$ clathrate has been studied by *in situ* high-pressure angle-dispersive x-ray powder diffraction using liquid He as pressure transmitting medium. The good quality of the diffraction data permitted refinement of structural and thermal parameters from Rietveld analysis. The results show that the first transition at 7 GPa is caused by the displacement of the Ba atoms in the Si_{24} cages. The cause of the second transition at 15 GPa, characterized by a dramatic reduction of cell volume, is not as clear. Theoretical calculations predicted an electronic topological transition of Fermi surface at this pressure. Analysis of the anomalously large Si thermal parameters suggested a highly disordered Si framework. This disordering is probably static and may be due to the presence of Si vacancies. The latter hypothesis is supported by electronic calculations on model disordered systems.

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INTRODUCTION

Since the report on the superconducting behavior of $\text{Ba}_8\text{Si}_{46}$, the properties of this compound and related semiconductor clathrates have been studied extensively.^{1–17} Very low compressibility in a Na-doped Si clathrate with the type-II structure was first reported,¹² which transforms into an amorphous phase at ~ 12 GPa. In contrast, the type-I Si_{46} clathrates of K (Ref. 13) and Ba (Ref. 14) are found to be stable at much higher pressure. X-ray diffraction (XRD) measurements show an isostructural phase transition characterized by a sudden reduction in the unit cell volume at about 13–15 GPa for $\text{Ba}_8\text{Si}_{46}$ (Ref. 14) and 23–25 GPa for K_8Si_{46} (Ref. 13) clathrates. Raman studies, however, revealed an additional “transition” for type-I $\text{Ba}_8\text{Si}_{46}$ (Ref. 15) and K_8Si_{46} (Ref. 17) clathrates at 7 GPa. It should be noted that there is no evidence of structural transition (i.e., change in crystal unit cell parameter and/or space group symmetry) associated with this proposed transition. *Ab initio* phonon band structure calculations for K_8Si_{46} suggested that K atoms are displaced from the center of the Si_{24} cages and are responsible for the transition at 15 GPa.¹³ It was speculated that a similar mechanism may be responsible for the $\text{Ba}_8\text{Si}_{46}$ transition¹⁵ at 7 GPa. The nature of the second isostructural transition at about 15 GPa detected by XRD (Ref. 14) and Raman (Ref. 15) measurements on $\text{Ba}_8\text{Si}_{46}$, however, is not as clear. A more recent XRD and x-ray absorption study¹⁸ attributed the transition to the rehybridization of the Ba atoms. This suggestion, however, does not explain the large volume reduction accompanying the phase transition. Therefore, the understanding of the mechanisms responsible for the successive isostructural transitions in type-I Si-clathrates remains a challenge. To reveal the nature of these unique transitions, it

is critical to know the evolution of the crystal structure with pressure by obtaining accurate structural parameters. For this purpose, we performed high quality *in situ* high-pressure angle-dispersive x-ray powder diffraction measurements on $\text{Ba}_8\text{Si}_{46}$ clathrate using liquid He as the pressure transmitting medium. He is perhaps the best pressure transmitting media to maintain quasihydrostatic condition up to at least 28 GPa.¹⁹ Reliable structural parameters may be determined from the high quality high pressure diffraction patterns by Rietveld refinement. First-principles calculations of the electronic structures and phonon spectra were performed to characterize structural changes, electronic properties and dynamical stability.

EXPERIMENTAL AND THEORETICAL DETAILS

Alloy ingots with a composition of $\text{Ba}_8\text{Si}_{46}$ were prepared by arc melting pure elements of 99.9999% Si and 99.8% Ba

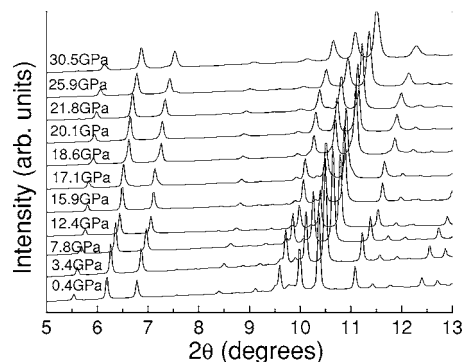


FIG. 1. Pressure dependence of the XRD patterns at various pressures for the type-I $\text{Ba}_8\text{Si}_{46}$ clathrate.

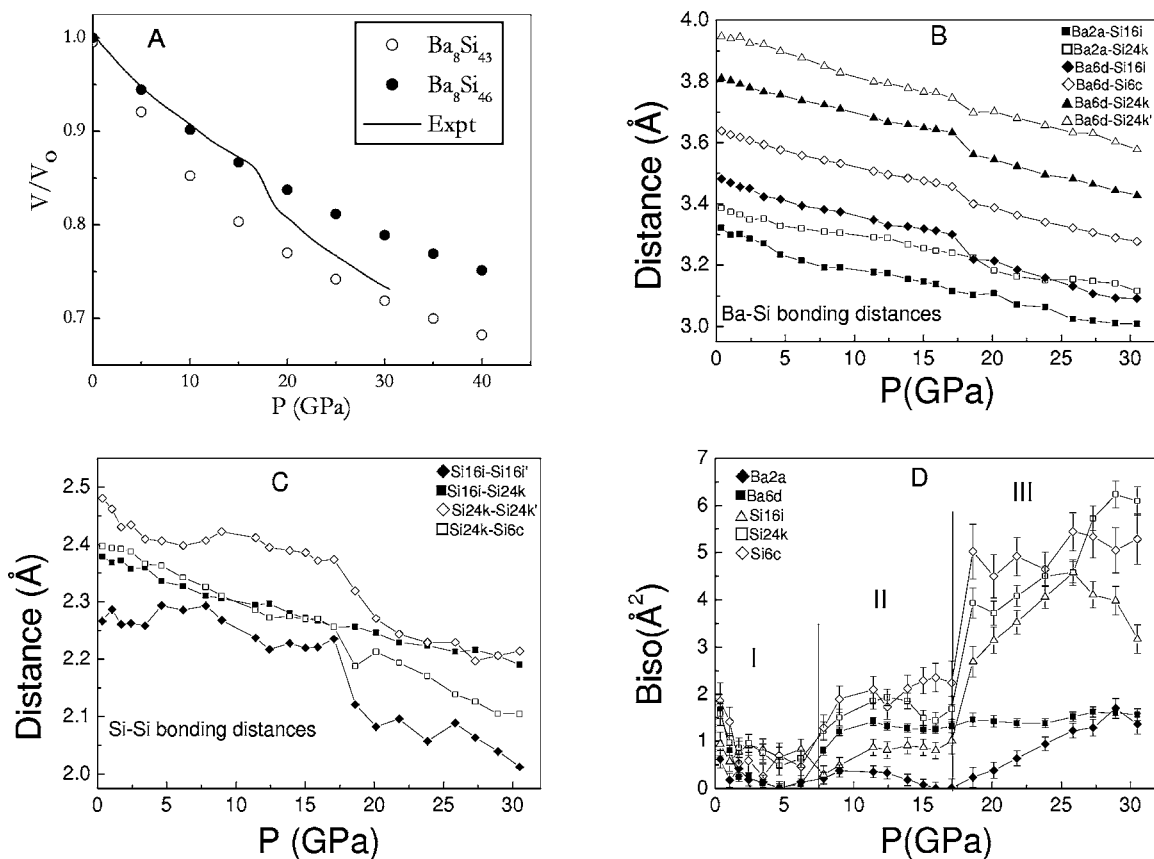


FIG. 2. Pressure dependence of various parameters, cell volume (a), interatomic distances (b) and (c) and thermal parameters (d), obtained from Rietveld refinements together with theoretical simulation data of cell volume for the type-I Ba_8Si_{46} clathrate. A comparison of the calculated equation of state for Ba_8Si_{46} and Ba_8Si_{46-x} ($x=3$) (see text) is also given in (a).

in a purified argon atmosphere. Type-I Ba_8Si_{46} clathrate sample was synthesised by high temperature and high pressure route reported in Ref. 20 at 3 GPa and 1173 K using a multianvil pressure apparatus with 8 mm cube pressure cells.²¹ High quality *in situ* high-pressure XRD measurements at ambient temperature using a Diamond Anvil Cell with liquid He as pressure transmitting medium were performed at BL10XU beamline, SPring8, Japan at a wavelength of 0.496 887 Å. A total of 25 diffraction patterns up to approximately 32 GPa were recorded using an image plate (IP). All high-pressure XRD patterns were refined by a local modification of the LHMP1 Rietveld refinement program,²² using the pseudo-Voigt profile function and Chebyshev polynomial background fitting. The high quality of the diffraction patterns with angular range of 25° permits the simultaneous refinement of the atomic positions and isotropic thermal parameters within acceptable statistics.

First principles electronic calculations and geometry optimization were performed mostly with the VASP package²³ using the projector augmented pseudopotentials (PAW) (Ref. 24) within the gradient correction density functional approximation.²⁵ Additional electron density of states calculations were performed with the all-electron full potential program WIEN2k.²⁶ For electronic band structure and density of states (DOS) calculations, Monkhorst-Pack k meshes of $6 \times 6 \times 6$ and $8 \times 8 \times 8$ were used grid for the electronic Brillouin zone (BZ) integration, respectively. At a chosen

volume all the atomic positions were fully optimized. Phonon band structures were computed with the supercell method described earlier.^{27,28} As demonstrated previously,²⁹⁻³² this approach provides reliable vibrational spectra when compared to experimental Raman and neutron vibrational density of states for a variety of semiconductor clathrates.

RESULTS AND DISCUSSION

Figure 1 shows the pressure dependence of the diffraction patterns up to 32 GPa. Although the Bragg peaks become broader at higher pressure, there is no new features and significant change in relative intensities which might indicate a change of the crystal symmetry. All the diffraction patterns can be indexed to the space group $Fd3m$. It is important to note that there is a significant shift of peak positions to high angles at about 17 GPa. In cubic Ba_8Si_{46} (Ref. 20) the unique Si atoms are located at three distinct Wyckoff symmetry sites: Si6c, Si16i and Si24k. The Ba atoms are assumed to locate at the centers of two “small” Si_{20} (pentagonal dodecahedron) cages (Ba2a) and six large Si_{24} (tetrakaidecahedron) cages Ba6d. Figure 2 shows the pressure dependence of the cell volume, interatomic distances, and thermal parameters obtained from Rietveld refinements. The cell volume and Ba-Si interatomic distances are found to decrease gradually with pressure up to about 17 GPa. At 17 GPa, an abrupt drop

in cell volume and interatomic distances are clearly observed. These results verify that the reduction in cell volume observed in previous experiments on K_8Si_{46} clathrate¹³ and $\text{Ba}_8\text{Si}_{46}$ clathrate¹⁴ is indeed an intrinsic phase transition rather than due to a nonhydrostatic effect. At pressures around 7 GPa, no anomaly in the cell volume, Ba-Si and (Si-Si) bond distances was observed. The only exception is that the distance between Si16i-Si16i', which does not seem to decrease with increasing pressure. An interesting observation is the thermal parameter as a function of pressure. Three different pressure regions marked by I, II, and III in Fig. 2(d) can be identified. At pressures below 7 GPa (region I), as expected, all the atom thermal parameters decrease with pressure. This is simply the result of the shortening of interatomic bond lengths under compression resulting in more repulsive potentials and, therefore, smaller, vibrational amplitudes. At about 7 GPa, the thermal parameters for Ba6d, Si24k, and Si6c increase with increasing pressure up to 12 GPa and becomes steady afterwards. It is interesting to observe that the thermal parameter for the Ba2a atoms in the small cages remain very small and have little variation throughout the pressure range from 7–17 GPa. The results indicate that the changes in Raman spectra observed at 7 GPa by (Ref. 15) *are only associated with Ba6d atoms located in the large cages*. At about 17 GPa, the thermal parameters for the Si atom increase significantly with increasing pressure from approximately 2 \AA^2 to 5 \AA^2 . On the other hand, the thermal parameter for Ba2a increases slightly and merges with that of Ba6d. The changes in the thermal parameters nicely follow the abrupt volume reduction at about 17 GPa and is consistent with the occurrence of a first order phase transition.

The calculated equation of state (EOS) for $\text{Ba}_8\text{Si}_{46}$ obtained from fitting the calculated total energies as a function of volume to the Murnaghan EOS (Ref. 33) is compared with experimental data in Fig. 2(a). As illustrated in Fig. 2, the calculated volume compression curve (V/V_0) agrees very well with experiment in the low pressure region up to 12 GPa. Significant deviation of the experimental volume ratios from the calculated results was observed for pressures higher than 17 GPa. Particularly, the calculated compressibility (change in volume with pressure) is much smaller than the experimental observation. A more detail examination of the calculated lattice constants and optimized atom positions with pressure is shown in Fig. 3. It is shown that there is a hint of discontinuity in the calculated lattice parameter at 14 GPa. Although the large observed volume compression was not reproduced, the calculated trends of the atomic coordinates are in agreement with the experimental data reported here and in a previous study.¹⁸ Specifically, the lack of pressure dependence of the x coordinate of Si16i and the y coordinate of Si24k and the slight increase of the z coordinate of Si24k above 20 GPa are reproduced correctly. The theoretical phonon band structures of $\text{Ba}_8\text{Si}_{46}$ at 0, 7, 35, and 42 GPa are shown in Fig. 4. No dynamical stability was found until the pressure reaches 42 GPa where frequencies of the transverse acoustic phonon branches around the M symmetry point become imaginary indicating that the clathrate framework is unstable. Incidentally the estimated pressure of 38 GPa is in good accord the observed onset of amor-

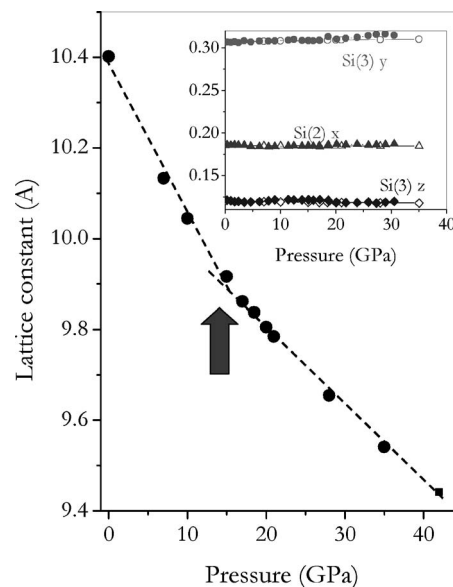


FIG. 3. Calculated unit cell dimension and Si positions for $\text{Ba}_8\text{Si}_{46}$ as a function of pressure. Note the small “kink” in the unit cell at ~ 14 GPa. (inset, open symbols: theory, filled symbols: experiment).

phization of $\text{Ba}_8\text{Si}_{46}$ at approximately 35 GPa.

Based on theoretical and experimental results, it is now possible to propose an explanation for the apparent “transition” observed at 7 GPa in the Raman and x-ray absorption spectra of $\text{Ba}_8\text{Si}_{46}$. As shown by the x-ray analysis, below 7 GPa, the unit cell parameter and the Si-Si, Ba-Si distances reduced smoothly with pressure. Theoretical calculations show a small transfer of electrons from the Ba to the Si framework ($0.018e$ for Ba2a—small cage and $0.03e$ for Ba6d—large cage) within this pressure range. The more positively charged Ba atoms is consistent with the observed 0.4 eV shift to high binding energy of the Ba $L_{II,III}$ edge.¹⁸ Around 7 GPa the Raman peaks at $50\text{--}60 \text{ cm}^{-1}$ was reported to be missing.¹⁵ Theoretical calculations have shown that this Raman band is entirely due to the vibrations of Ba located in the large cage (i.e., Ba6d).³² It is worth noting that from a factor group analysis, Ba vibrations in the small cages are not Raman active.³² Since Raman spectroscopy measures the change in polarizability, the *disappearance* of the Raman band indicates that there are substantial changes in the polarizability of the Ba6d atoms. It is found in Fig. 2(d) that the isotropic thermal parameter of Ba6d increases to approximately 1.4 \AA^2 at 7 GPa. The isotropic thermal parameter (B) is related to the mean-square vibrational amplitude $\langle u \rangle$ ($B = 8\pi^2\langle u \rangle^2$). The estimated average (vibrational) displacement of Ba from the center of the large cage is 0.14 \AA . This is to be compared with the mean Ba-Si distance of 3.58 \AA in the large cage at 7 GPa. The larger vibrational amplitude of the Ba suggests stronger interactions with the Si framework atom. Since only the thermal parameter of Ba6d is affected so are the Raman active modes associated with these atoms. A more positively charged Ba results in a tighter ion and reducing the Raman intensity. A plausible explanation for the change in the Ba polarizability may be related to the electronic structure where it was found that the conduction mini-

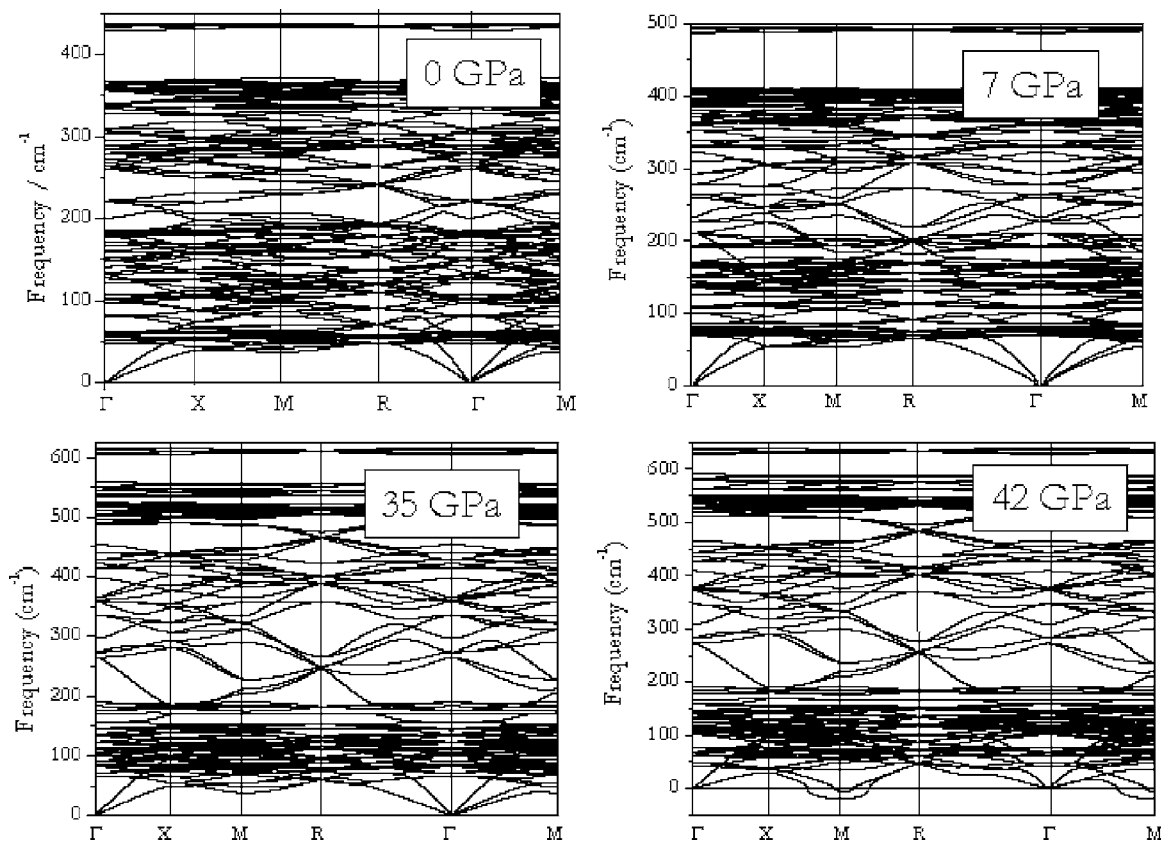


FIG. 4. Calculated phonon band structure for $\text{Ba}_8\text{Si}_{46}$ at 0, 7, 35, and 42 GPa.

imum at the R symmetry touches the Fermi level at 7 GPa. As will be discussed later (*vide supra*), the conduction minimum at the R point is predominantly $\text{Ba}6d$ in character. This might suggest the onset of a rehybridization of Ba atoms that changes the valence electron distribution thus affecting the polarizability.

The mechanism for the transition is more intriguing. The calculated electronic band structure of $\text{Ba}_8\text{Si}_{46}$ at 0, 7, 17, and 21 GPa are shown in Fig. 5. The Fermi level is located at the conduction band of the Si_{46} cage, indicating a metallic n -type doping character by the introduction of the Ba atoms. It is found that starting from 7 GPa, the electron bands near the R symmetry point (indicated by the red circle) approach the Fermi level from above with increasing pressure. At 14–17 GPa, the band crossings over the Fermi level are largely completed. This results in a significant change in the Fermi surface creating an electron hole around R . This phenomenon is akin to the electronic topological transition (ETT).³⁴ Incidentally, the theoretical calculations also predicted a small “kink” in the unit cell parameter at 14 GPa (Fig. 3). The electronic bands around the R symmetry point near the Fermi level compose of majority $\text{Ba}6d$ character [Fig. 5(d)]. Therefore, the $\text{Ba}6d$ contribution to the filled and empty bands near the Fermi level is expected to increase. This is confirmed by the analysis of the Ba $L_{1,III}$ near edge x-ray absorption spectra which show an increase in the intensity due to $p \rightarrow d$ transitions.¹⁸ Although the theory succeeded in predicting an anomaly, the predicted change in the cell parameter is much smaller than the observed. To explain

this discrepancy, other possible mechanisms must be considered. Particularly interesting is that the thermal parameters for the Si atoms increase dramatically from 2 \AA^2 to 5 \AA^2 . The corresponding increase in the mean amplitude of vibration is from 0.16 \AA to almost 0.25 \AA . The very large vibrational amplitude is unphysical and cannot be explained from the electronic structure of $\text{Ba}_8\text{Si}_{46}$. This observation is contrary to the general view that vibrational amplitude should become smaller with increasing density (i.e., pressure). It is unlikely that the Si atoms are dynamically disordered. The other explanation is that the framework Si atoms are statically disordered with a mean distribution around the crystallographic symmetry sites of $\sim 0.25 \text{ \AA}$. This interpretation may not be implausible. In addition to the repulsive interactions due to compression the donation of electrons from the electropositive Ba to the Si network will further weaken the already saturated Si-Si bonds. It has been shown previously³⁵ at 17 GPa, elemental Si is stable in the simple hexagonal Si V phase in which the Si rehybridized from the ambient pressure sp^3 to sp bonding. The rehybridization may lead to softer interactions and, consequently, reduce the compressibility resulting in an abrupt collapse in the volume of the unit cell and perhaps induce positional disordering in the Si atoms. In principle, this hypothesis can be tested via the calculated of the electron charge density extracted through the maximum entropy method (MEM) (Ref. 36) directly from the diffraction data. However, quality of the experimental diffraction patterns needs to be carefully examined before attempting such analysis. If hybridization indeed occurred at

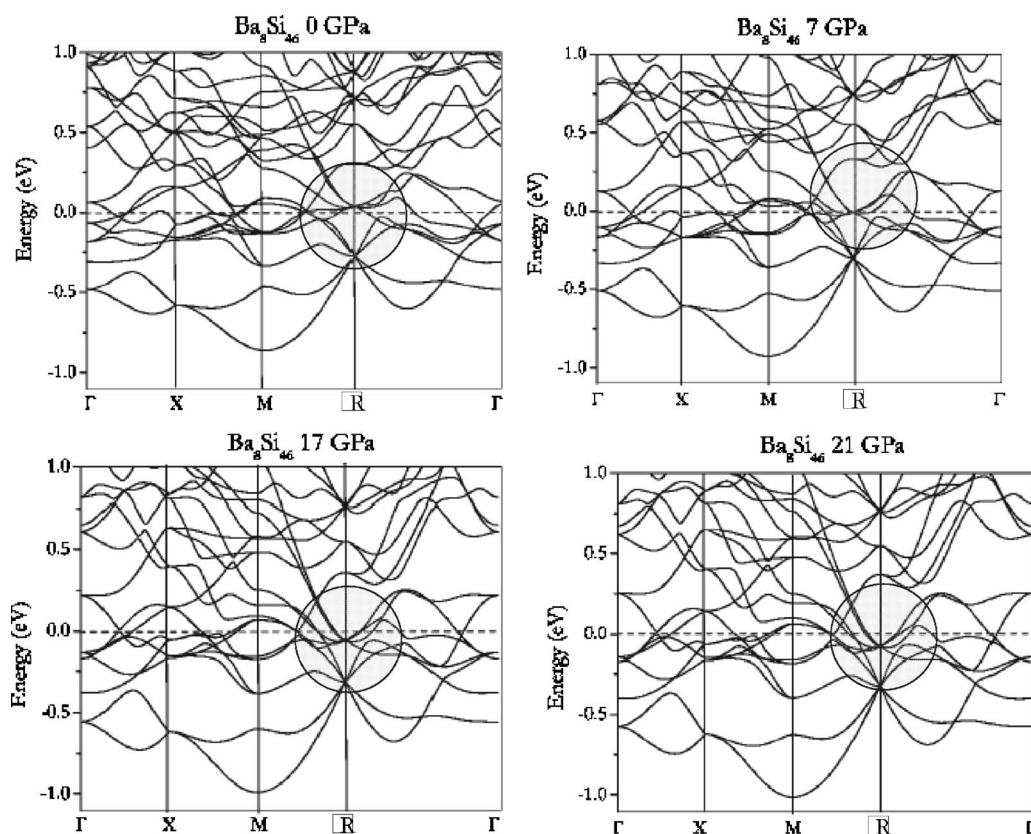


FIG. 5. Calculated electronic band structure for $\text{Ba}_8\text{Si}_{46}$ at 0, 7, 17, and 21 GPa. Note the conduction band minimum at the R symmetry point moves closer to the Fermi level with increasing pressure and then drop below Fermi level at 17 GPa signaling an ETT.

the Si6c sites, it is expected that phonon softening should be observed in the phonon band structure above 15 GPa. This is not supported in the present calculations.

There may be an alternative interpretation. It is well known that in a structural refinement the thermal parameter is highly correlated to the site occupancy of the atom. Larger thermal amplitude indicates a higher level of disorder. It is possible that the disorder may be due to the appearance of vacancy Si sites. In a sense, the Si atoms are being “squeezed” out of the framework. The occurrence of framework atom vacancies is not uncommon in semiconductor clathrates. Theoretical calculations indicated³⁷ the vacancy is likely located in the 6c sites. For example, in $\text{Cs}_8\text{Sn}_{44}$, some of the Sn atoms disappeared from the 6c sites. In $\text{I}_8\text{Si}_{44}\text{I}_2$, two of the Si6c atoms are replaced by I.³⁸ To test this hypothesis, electronic structure calculations were performed on $\text{Ba}_8\text{Si}_{46-x}$ with some of the Si atoms removed from the framework Si6c sites. The results of the calculations are reported in Fig. 2(a). It is shown that the calculated equation of state for $\text{Ba}_8\text{Si}_{46-x}$ ($x=3$) with Si defects is more compressible than $\text{Ba}_8\text{Si}_{46}$. In fact, the calculated EOS is in much better agreement with the experimental observation for pressures above 16 GPa. In view of the anomalously large ther-

mal parameters of the Si atoms determined from Rietveld refinement, the existence of Si vacancy sites is a strong possibility. It should be mentioned that additional features have been observed in the Raman spectra of $\text{Ba}_8\text{Si}_{46}$ at pressures above 12 GPa. The spectra become more obscure and most of the features above 320 cm^{-1} “disappear” at 15 GPa and above. These observations are indicative of disordering in the $\text{Ba}_8\text{Si}_{46}$ structure.¹⁵ It is worth noting that all the experimental thermal parameters of Si atoms become anomalously large at pressure higher than 15 GPa. Therefore, if there were Si vacancies, it is not restricted to the 6c sites.

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