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热电笼状物声子作用对其反常比热容的影响

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摘 要: 笼状物材料具有极低的晶格热导率,表现出非常优秀的热电性能. 但是,笼状物中束缚在笼子中的原子与笼子的相互作用形式尚不明确,这种相互作用与其反常热力学性质的关系仍有很多争议. 使用从头算晶格动力学计算方法计算笼状物 $Ba_8Ga_{16}Ge_{30}$(BGG)的声子以及比热容,利用同位素 Ge-76 替换的方法研究束缚原子与笼子的相互作用. 结果表明,束缚原子与笼子之间存在着明显的耦合作用,这种耦合作用对笼状物反常热力学行为的产生具有重要意义.

关键词: 热电材料; 从头算晶格动力学计算; 笼状物; 声子作用; 比热容
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Impact of the phonon interactions on the anomalous specific heat of thermoelectric clathrates

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Abstract: Clathrates are extraordinary thermoelectric materials due to their low thermal conductivity. However, it is generally assumed that the atoms captured in the cages, so-called the guests, act as "rattlers" inducing disordered lattice dynamics and unusual thermal properties. Here, the isotope Ge-76 has an evident influence on the phonons and the heat capacity of $Ba_8Ga_{16}Ge_{30}$ (BGG) by using *ab initio* lattice dynamics calculations. The results verify the intense coupling between the guest and host lattice which contributesto the anomalous specific heat. This finding paves the way for understanding the microscopic mechanism of clathrates and designing the thermoelectric materials with high performance.

Keywords: Thermoelectric materials; *Ab initio* lattice dynamics calculations; Clathrates; Phonon interactions; Specific heat

1 Introduction

The semiconductor clathrates composed of networked cages, so-called the host, filled by guest atoms are extraordinary thermoelectric functional materials[1-2]. Clathrates show not only high thermoelectric power (see beck coefficient) but also glass-like low thermal conductivity while the electric conductivity is high, leading to heat flow transferring into electron energy efficiently. The phenomenon is well known as "phonon-glass electron-crystal" (PGEC)[3]. It is noted that, al-

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though clathrates crystallize in the high-symmetry cubic structure, they show glass-like specific heat. The specific heat displays a broad peak around 10 K[4-5], which is supposed to be a constant in terms of C/T^3 as function of T according to the Debye T^3 law. This peak almost coincides with the boson peak observed in amorphous materials, such as polymers and silica glasses[6-7]. The mechanism of such phenomenon has attracted extensive attentions.

Initially, it was proposed that the guests loosely bound in the oversized cages vibrate as independent "rattlers"[8]. The rattling guests scatter the heat-carrying phonons of the host lattice and efficiently reduce the thermal conductivity[9-11]. Moreover, the "rattlers" contribute excess density of state over those of Debye phonons, giving rise to the anomalous boson-like peak in the specific heat[12-14]. However, the decoupled dynamics of the guests were questioned recently[15-17]. By employing the improved neutron spectroscopy experiments and *ab initio* calculations, Koza *et al.*[16] found that there are pronounced guest-host couplings in cage-structured skutterudites. More recently, on the basis of three-phonon interactions, Tadano *et al.*[17] reproduced the glass-like thermal conductivity using first-principles calculation and claimed that the anharmonic effect induces the thermal conductivity in clathrates. These findings conflict with the "rattler" scenario. Therefore, the mechanism of the unusual thermal properties of clathrates is still under debate.

Here, using *ab initio* lattice dynamics calculations on clathrates $Ba_8Ga_{16}Ge_{30}$ (BGG), we analyze the dynamics of the guest to gain a deeper understanding on the anomalous specific heat. Because the dynamical properties are relevant to the mass, isotope substitution is employed in our study. In particular, we study the isotope effect on the phonons and the specific heat by substituting natural Ge by isotopic Ge-76, and decompose the specific heat of BGG. As discussed below, we observe guest-host coupling in clathrates and find out that the guest-host interactions contribute to the boson-like peak in the specific heat.

2 Calculation method

The electron-structure of BGG is calculated with the framework of the density-functional theory (DFT)[18-19] using the Vienna *ab initio* Simulation Package (VASP)[20]. The projector-augmented wave (PAW) pseudopotentials[21-22] is used for the description of the electronic state. For the exchange-correlation functions, we employed the local-density correlation (LDA)[23]. The energy cutoff of 400 eV was adopted and the Brillouin zone was performed with $4\times4\times4$ Γ centered Monkhorst-Pack k grids[24]. In the relaxed configuration, the force was smaller than 0.1 meV/Å. The phonon calculations are carried out using Phonopy package[25] based on the lattice dynamics theory[26]. The force-constant matrices are calculated by displacing an atom from its equilibrium position by 0.02 Å using finite-displacement approach[27]. The DOS-related quantities are evaluated by the smearing method[28]. The results of isotope-substituted BGG are calculated by changing the mass matrix of the dynamical matrix, which can be constructed from the force-constant matrices, under the assumption that the electron structure is mass independent.

Using the phonons calculated above, the specific heat of BGG ($C_{p,\mathrm{BGG}}$) can be calculated in quasi-harmonic approximation[29-30]. To investigate the nature of the boson-like peak, we decompose the contribution of the guests ($C_{p,\mathrm{Ba}}$) from $C_{p,\mathrm{BGG}}$. We first calculate the specific heat of unfilled clathrates ($C_{p,\mathrm{GG}}$). Since the GG cage without Ba is unstable, $C_{p,\mathrm{GG}}$ can be obtained from the force constants matrices of BGG by setting the terms involving the Ba atoms to zero according to the procedure reported by Tadano *et al.*[17]. Through this way, we can turn off the guest-host interactions of BGG. Therefore we obtain the decompose of $C_{p,\mathrm{Ba}}$, which is the difference between $C_{p,\mathrm{GBG}}$ and $C_{p,\mathrm{GG}}$(contribution without Ba).

$$\frac{C_{p,\mathrm{Ba}}}{N_{\mathrm{Ba}}}=\frac{C_{p,\mathrm{BGG}}}{N_{\mathrm{BGG}}}-\frac{C_{p,\mathrm{GG}}}{N_{\mathrm{GG}}} \quad (1)$$

where N_i is the number of i atom in the unit cell BGG.

3 Results and discussion

The symmetry of BGG is Pm $\bar{3}$n, as shown in Fig. 1. According to the group theory, the Raman active phonons are $3A_{1g}+8E_g+9T_{2g}$. Fig. 2 (a) and (b) show the Raman active phonons in E_g and T_{2g} irreducible representations. The mode marked by "A" is only observed in Raman spectra since the guests in the 6d-cages of experiment sample rotate at the off-center position[31]. The modes, contributed mainly by the guests in the 6d-cages, are marked by "G". It can be seen that the calculated phonon modes agree well with experiment data.

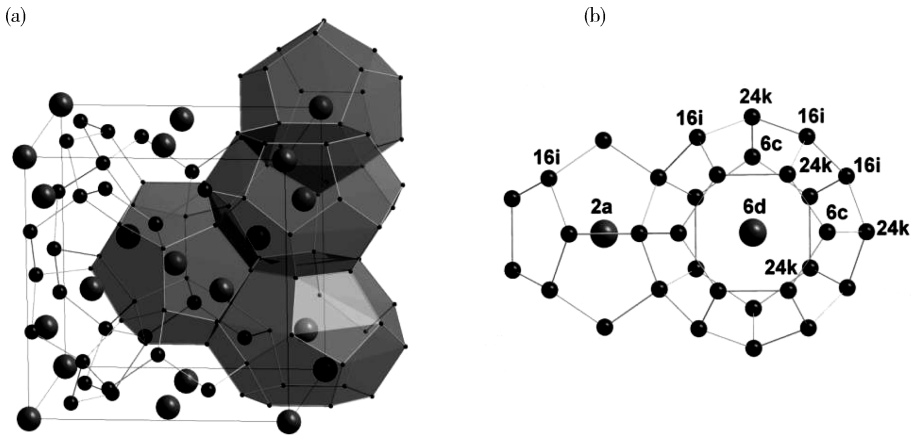

Fig. 1 (a) Structure of BGG which crystallizes in cubic space group Pm $\bar{3}$n. Ba are represented by grey and magenta spheres. Ga, Ge atoms are represented by black spheres. (b) The cages are formed by crystal sites with Wyckoff positions 24k, 16i and 6c. Ba are placed at the 2a, 6d positions

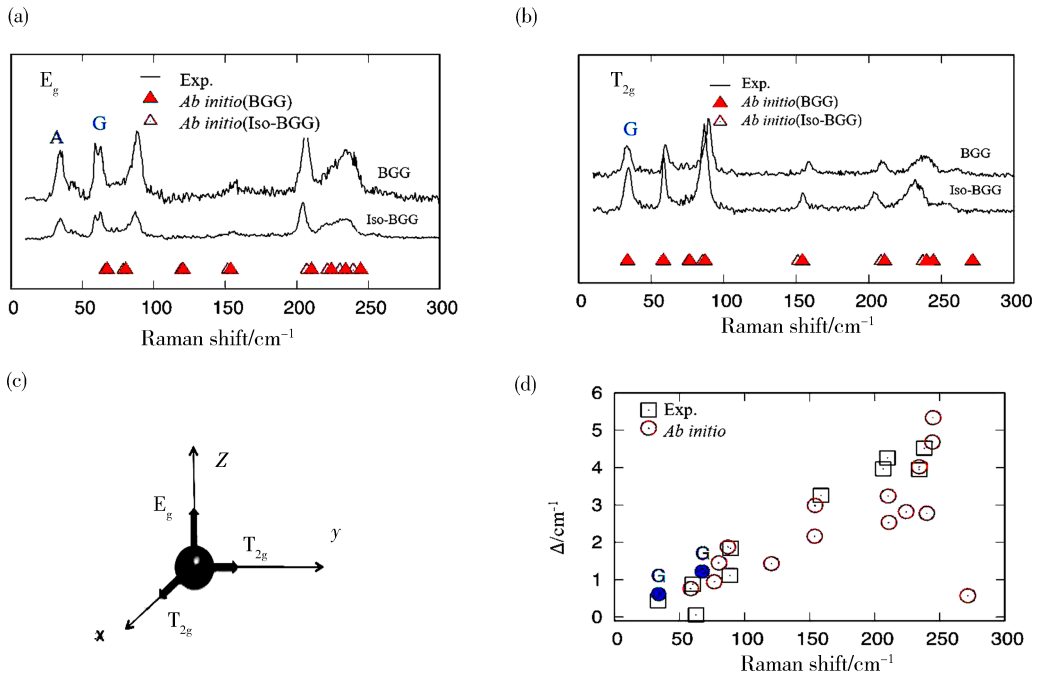

Fig. 2 (a~b) Calculated Raman active phonons of BGG (open triangle) and isotope substituted BGG (filled triangle), in comparison with the corresponding Raman spectra in experiment (black curves). The peaks marked by G and A indicate allowed guest mode. (c) Vibration of atoms of E_g, T_{2g} modes. (d) Experimental (square) and calculated (circle) isotope effects on phonons. The isotope effect is represented by Δ, difference of the frequencies of BGG and isotope substituted BGG. Experimental values from Ang *et al*.[32]

The isotope effect on the Raman active phonon modes is studied and shown in Fig. 2(d). The trend of the calculated isotope effect agrees well with experiment, except the mode at 271 cm^{-1} which corresponds to the vibration of Ga atoms positioned at 16i sites with large amplitude. It demonstrates the accuracy of our phonon calculations. Interestingly, germanium isotope substitution reduces the guest vibration in both E_g and T_{2g} irreducible representations. Because the interatomic potential and force constant are harmonic and independent of the isotope mass in our calculations, we think such properties might be attributed to guest-host coupling.

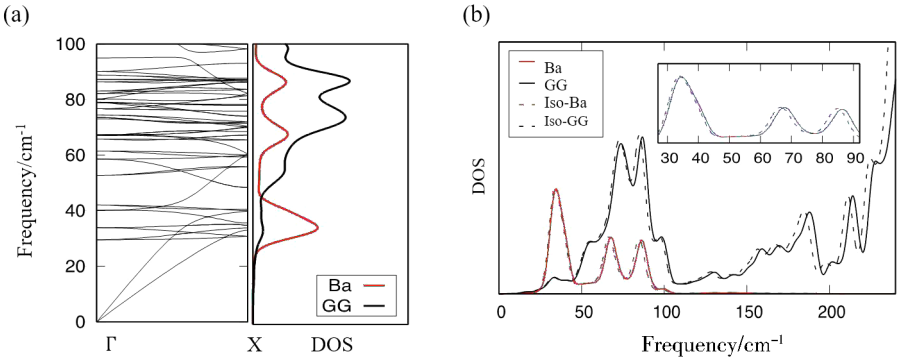

Fig. 3 (a) Calculated phonon dispersion and DOS of BGG; (b) isotope effect on the DOS. The solid lines represent the DOS of BGG, the dotted line represent that of isotope substituted BGG

To further investigate the guest-host coupling, we show the phonon dispersion and the DOS in Fig. 3(a). It can be seen that the modes of the guests, in the range from 0 to 100 cm^{-1}, have obvious contributions from the hosts, suggesting significant correlated motion between the guest and the host vibration. Fig. 3(b) shows the germanium isotope effect on the DOS of BGG. Since the lattice vibration is relevant to the isotope mass, that is heavier isotopes display smaller vibration energy than the lighter, the DOS of the isotope substituted BGG shifts to lower frequency. Significantly, the reduction in the vibration frequency, both of the guests and the hosts, happens in the whole frequency range. Keeping in mind that the interatomic potential and force constant are independent on the isotope mass, we conclude that the germanium isotope effect on the guest vibration is dominated by the guest-host coupling. Comparing to the independent "rattler" model, which ignores the correlated motion of the guests and the hosts, we can further investigate the role of the guest-host interactions on the boson-like peak.

Fig. 4(a) shows the calculated $C_{p,BGG}$ and its decomposed components. The calculated $C_{p,BGG}$ is in quite good agreement with the experimental $C_{p,BGG}$, confirming the existence of the guest-host coupling. To further investigate the role of the guest-host coupling, we extract the specific heat contributed by the guest-host interactions ($C_{p,Ba}$) according to equation (1). $C_{p,Ba}$ involving guest-host interactions reproduces the boson-like peak successfully, while $C_{p,GG}$ involving host-host interactions display a plateau, indicating that the guest-host interactions contribute to the origin of the boson-like peak in specific heat. To gain more insight into the correlation between the guest-host coupling and the boson-like peak, we show the germanium isotope effect on $C_{p,BGG}$ and $C_{p,Ba}$ in Fig. 4 (b). At temperature $T=11$ K, the peak of isotope substituted BGG increases in amplitude by about 24 $\mu J \cdot mol^{-1} \cdot K^{-4}$, in contrast, the magnitude of $C_{p,Ba}$ peak increases by 17 $\mu J \cdot mol^{-1} \cdot K^{-4}$. This suggests that the boson-like peak of $C_{p,BGG}$ is mainly driven by guest-host coupling, leading to isotope effect on $C_{p,Ba}$.

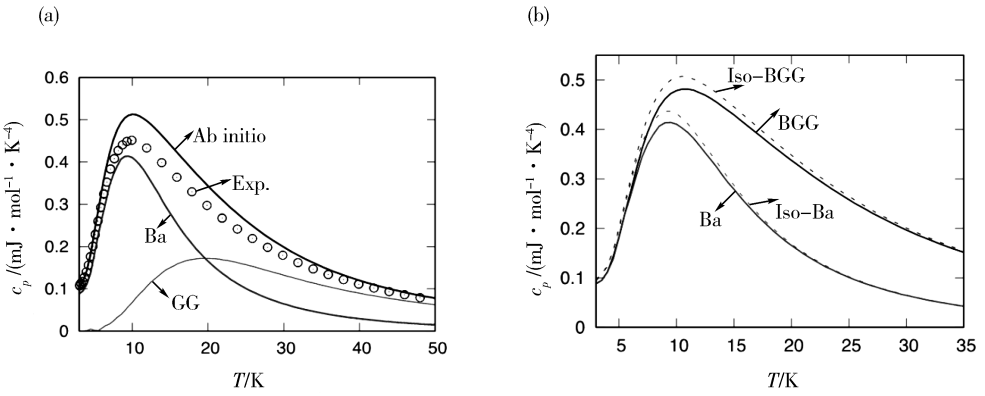

Fig. 4　(a) $C_{p,\mathrm{BGG}}$ and its decomposed components $C_{p,\mathrm{GG}}$, $C_{p,\mathrm{Ba}}$. The calculated $C_{p,\mathrm{BGG}}$ agrees well with the experimental data[32]. (b) Germanium isotope effect on $C_{p,\mathrm{BGG}}$ and $C_{p,\mathrm{Ba}}$

4　Conclusions

In summary, we investigated the microsoft mechanism of BGG clathrates. We firstly applied germanium isotope substitution to discuss the dynamics of the guest atoms, and further studied the origin of the boson-like peak by decomposing the specific heat. An important conclusion of our work is that there are obvious guest-host couplings in the clathrates. The isotope effect on phonons indicates that the guests cannot be considered as independent "rattlers". On the contrary, there is pronounced correlated motion between the guests and the hosts. Considering the guest-host coupling, we obtain the specific heat of BGG, which displays the boson-like peak and agrees well with experiment. By decomposing the specific heat of guest contribution from that of BGG, we found that the guest-host interact ions contribute significantly to the boson-like peak, which was not observed for the independent rattling scenarios. Therefore, the isotope effect is of crucial importance to uncover the microscopic mechanism of clathrates.

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