Universal van der Waals-type interactions in rattler containing cage materials

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Introduction

The rattling phenomenon might be first described by A. J. Sievers and S. Takeno in 1965, when they observed an anomalous peak of Li in KBr:LiBr at low frequencies.1 Recently, rattling behavior has been commonly observed in filler containing cage materials, such as Al2V5 type intermetallides,2 brownmillerite,3 skutterudite,4 pyrochlores5 and clathrate.6,7 Different from the Li-rattlers, the fillers (or guest atoms) in cage compounds are accommodated inside a periodic array of cages and can be quantitatively described. Fig. 1 shows a rattling containing cage, where the cage atoms are connected by covalent bonds, providing a strong wall and an oversized room for the guest atom. Since a guest atom is only weakly interacting with the surrounding cage atoms, it normally shows an anomalous low energy (ALE) frequency and a large atomic displacement parameter (ADP). Although showing anharmonicity, the ALE modes can be approximately described by the Einstein model, where guest atoms are treated as Einstein oscillators with a characteristic energy of \( \omega_E \). Rattling ALE phonon modes are scientifically important for: (1) their coupling with conduction electrons, giving rise to superconductivity,8 and an modification of electron effective mass;9,10 and (2) their coupling with propagating phonons, leading to an enhancement of scattering probability and consequent low thermal conductivity for thermoelectric applications.11,12

In the passed decades, the rattling phonon modes have been both experimentally and theoretically studied. The direct evidence has been provided by the phonon dispersion relationship of a type-I clathrate \( \text{Ba}_3\text{Ga}_{16}\text{Ge}_{30} \), derived from inelastic neutron scattering measurements.13 The rattling phonon modes are optical-branch-like at around 5 meV, lower than the top of acoustic phonon branches, giving rise to ALE peaks in the derived phonon density of states (PDOS). The ALE vibration modes have also been detected and discussed by Raman spectroscopy,14 optical conductivity,15 heat capacity (HC),16 and temperature dependent ADP obtained from crystallographic refinement of x-ray/neutron diffraction data.17 These experiment results have established the validity of the Einstein model for the description of the ALE modes; however exceptions were found for guest off-centered modes,18,19 which were rather anharmonic and beyond the scope of the Einstein model and the present discussion. In addition, many theoretical investigations have been performed as well, aiming at unveiling the rattling phonon associated phonon static and dynamic properties.20,21 Nevertheless the origin of the low energy modes was not clear.

In our previous work,18 we addressed a van der Waals-type interaction between a filler and its surrounding cage framework as the origin of the rattling ALE modes by focusing only on the 6d parallel modes in type-I clathrates.
In the present study we extend our scope to the other two modes in type-I clathrates (2a and 6d perpendicular modes, refer to Fig.2 for description of the modes) and the rattling modes in skutterudites and pyrochlores to unveil that the three dimensional (3D) van der Waals interaction is universal for rattler containing cage materials. Force constants, derived from the characteristic energies of guest atoms, are shown to vary exponentially with the free space of guest atoms \(R_{\text{free}}\) for each type of rattling mode. Different exponential parameters are obtained for different types of rattling modes, indicating that, besides space parameters discussed previously, chemical environment around guest atoms is another important factor that influences the guest-host interactions. The 3D van der Waals-type interaction, which coexists with the strong interatomic covalent interaction of framework atoms, significantly modifies the physical properties of a cage material via phonon-phonon and electron-phonon interactions, and provides a platform to study superconductivity and thermoelectricity.

Analyses method

A. Vibration modes and data collection

The current research is concerning the ALE vibration modes of the rattler in cage compounds. The situation for skutterudite and pyrochlore is simpler, because they are composed of single type of cages and have only one guest-vibration mode (as shown in Fig.3). However, type-I clathrate, which contains two type of cages, is much more complicated. As shown in Fig.2 there are three guest modes: 2a, 6d\| and 6d\perp modes, which are shown by the blue cage, black arrow and red arrow in the orange cage, respectively. Here 2a and 6d represent the crystallographic sites on the cage centers, \| and \perp are the directions with respect to the six-atom ring of the tetrakaidecahedral cage.

Different ALE modes have different characteristic energies \(\omega_E\), depending on the chemical environment and the relative free space that rattlers can move. In principle, the vibration energies can be directly detected by INS, Raman spectroscopy and heat capacity measurements. However, if \(\omega_E\) is not low enough, and close to the top of an acoustic phonon branch, where the acoustic phonon becomes less propagative (the acoustic phonon branch becomes flat at the Brillouin zone edge), \(\omega_E\) cannot be precisely obtained from these experiment techniques, because the contributions from van Hove singularities cannot be extracted. We have exemplified the situation in the heat capacity analyses for K\(_4\)Si\(_3\)As\(_9\), where the number of ALE modes obtained from data fitting exceeds what we expect from the number of guest atoms, showing clearly the contributions from van Hove singularities.\(^{18}\) In order to obtain a correct value for \(\omega_E\), temperature dependent ADP of a guest atom is useful.\(^4\) Therefore, the \(\omega_E\)’s in the present analyses are mainly derived from ADP data from literatures (Refs.\(^{10}\)-\(^{18}\)) for the three modes of type-I clathrates and the guest modes of skutterudites. The \(\omega_E\)’s for pyrochlores are taken from heat capacity data reported by Hiroi et. al.\(^{42}\) The data are summarized in table I.

B. Van der Waals potential model and harmonic approximation

To interpret the guest vibration modes, we introduce a modified Morse potential as we did previously.\(^{18}\) As shown in Fig.4, the potential of a guest atom inside a cage can be simplified by pair-wise potentials and expressed by,

\[ V_\ell(r) = V(R + r) + V(R - r) = ae^{-nb(R+r-r_e)} - ane^{-b(R+r-r_e)} + ae^{-nb(R-r-r_e)} - ane^{-b(R-r-r_e)} \]  

(1)

where \(R\) is shown in Fig.1 and can be viewed as a cage radius, \(r_e\) is the equilibrium distance and can be estimated by \(R_{\text{host}}^{\text{guest}} + R_{\text{host}}\) using van der radii of atoms; \(n, a \) and \(b \) are free parameters with \(n \gg 1\). The expression can be simplified by introducing \(R_{\text{free}} = R - r_e\):

\[ V_\ell(r) = ae^{-nb(R_{\text{free}}+r)} - ane^{-b(R_{\text{free}}+r)} + ae^{-nb(R_{\text{free}}-r)} - ane^{-b(R_{\text{free}}-r)} \]  

(2)

What we are focusing on is the potential minimum, where a guest atom is on the center and \(r\) equals to zero. One can easily derive the following equations,

\[ V_\ell(r = 0) = 2a(e^{-nbR_{\text{free}}} - ne^{-bR_{\text{free}}}) \]  

(3)

\[ V_\ell'(r = 0) = 0 \]  

(4)

\[ V_\ell''(r = 0) = 2anb^2(ne^{-nbR_{\text{free}}} - e^{-bR_{\text{free}}}) \]  

(5)

A potential minimum requires \(V_\ell'' > 0\), so the cage radius should satisfy the following criteria,

\[ R < R_e = r_e + \frac{\ln(n)}{nb - b} \]  

(6)

otherwise, the central position is not stable, and two potential minima arise near the center.

Under harmonic approximation, the force constant \(F_c\) of a harmonic oscillator can be expressed by \(V_\ell''(r = 0)\), with the assumption that the repulsive term is much larger than the attractive term.

\[ F_c = 2anb^2(ne^{-nbR_{\text{free}}} - e^{-bR_{\text{free}}}) \approx 2anb^2e^{-bR_{\text{free}}} \]  

(7)

Experimentally, \(F_c\) can be estimated by the harmonic oscillator model that \(F_c = m\omega_E^2\). Therefore, the simple exponential relationship can be tested by experiment data.
1.58 Å was estimated using R was defined as the distance between a guest atom were used for R was estimated using R was defined as the distance between a guest atom

C. Unified picture of different ALE modes in cage compounds

As shown in Fig. (b-c), the exponential behavior, \( F_C = A e^{-BR_{\text{free}}^2} \), holds for each guest mode in type-I clathrate. Here \( A = 2a n^2 b^2 \) and \( B = nb \), corresponding to the parameters derived earlier. \( R_{\text{free}} \) was estimated using \( R_{\text{free}} = R_{\text{guest}} + R_{\text{host}} \), and \( R \) was defined as the distance between a guest atom and its nearest neighbour \( R_{\text{guest}} \) van der Waals radii were used for \( R_{\text{guest}} \) and \( R_{\text{host}} \) and they are: 1.40 Å(Sr), 1.57 Å(Ba), 1.01 Å(Na), 1.32 Å(K), 1.44 Å(Rb), 1.61 Å(Cs), 1.27 Å(Ca), 2.10 Å(Si), 2.11 Å(Ge), 2.17 Å(Sn), 1.87 Å(Ga), 1.39 Å(Zn), 1.4 Å(Cu), 1.63 Å(Ni), 1.72 Å(Ag), 1.66 Å(Au), 1.58 Å(Cd), 1.93 Å(In), 1.84 Å(Al), 1.52 Å(O) and 2.06 Å(Sb). Irrespective of different vibration modes, the component elements are same for different cages, therefore we assume \( nb \) keeps the same value for each case, and \( a \) is variant depending on the effective number of guest-host pairs (the total potential is the sum of the component pairwise potentials). In the fitting, we set \( B = 3.0 \), which we reported previously. The fitting parameters \( A \) and \( B \) are listed in Table II. For the 6d\( \parallel \) mode, the result from ADP data is consistent with the result from heat capacity data. The 2a and 6d\( \perp \) modes show similar behavior but are much stronger than the 6d\( \parallel \) mode. The difference will be discussed later on, but it is noteworthy that it does not originate from space parameters, which have been already renormalized by \( R_{\text{free}} \).

For skutterudite and pyrochlore, although lack of sufficient data point, the exponential dependence can also be clearly seen in Fig. (b-c). Obviously, the guest-host interaction is much stronger than that in type-I clathrate, this might be the reason that rattling vibrations in some of these compounds have much higher energies and can not be clearly distinguished from other high energy non-dispersive phonon modes.

Discussion

To have a deep insight into the guest-host interactions based on the van der Waals potential model, we consider the nearest cage atoms as primary atoms that strongly interact with the guest atom. The closest interspace for each cage is shown in Fig. (a) and Fig. (b). In type-I clathrate, for both dodecahedral and tetraakisdecahedral cages, guest atoms have eight nearest neighbors; however the closest interspaces are in different shapes: a cube and a twisted cuboid, respectively. Therefore the 2a mode inside the cube is isotropic, while the 6d mode inside the twisted cuboid is anisotropic and splits into a 6d\( \parallel \) mode and a 6d\( \perp \) mode. The total guest-host interactions inside the tetraakisdecahedral cage can be resolved along 6d\( \parallel \) and 6d\( \perp \) directions, as shown by the arrows in Fig. (b-c). According to the geometry of the twisted cuboid, the strength of the interaction along 6d\( \parallel \) direction is weaker than that along 6d\( \perp \) direction, and the ratio is around 0.62, which is very close to the ratio of the fitting parameters (shown in Table II). This is not just a coincidence, but rather indicates that the proposed van der Waals interaction works well for the rattling system, and the interaction is closely associated with the effective number of pairwise potentials (or the coordination number) and the cage geometry.

In skutterudite and pyrochlore, the situation is very different, not only in the number and geometry of the primary cage atoms, but also in the component elements. Correspondingly, the fitting parameters \( A \) and \( B \) are very different. The cage of clathrate is mainly composed of Si/Ge/Sn, while the cage of skutterudite is mainly composed of P/As/Sb and the cage of pyrochlore is mainly...
interactions, such as ionic interactions, in addition to the large electronegativity, which may introduce additional composed of O. The elements in the later cases have much larger electronegativity, which may introduce additional interactions, such as ionic interactions, in addition to the principal van der Waals interactions. Under such an assumption, the guest atoms should be more easily to be off-centered, and this is true for pyrochlore compounds, while skutterudite cages are usually very small, so off-centered guest atoms were rarely observed. This conclusion can be supported by the critical radius estimated earlier as shown in equation [5]. The large $nb(B)$ values

| Type-I Clathrate | compounds | vibration $\omega_E$ (K) | Ref. | compounds | vibration $\omega_E$ (K) | Ref. |
|------------------|-----------|--------------------------|-----|-----------|--------------------------|-----|
| Ba$_8$Al$_{16}$Si$_{30}$ | Ba(6d∥) | 68 ADP$^{22}$ | Ba$_8$Al$_{16}$Ge$_{30}$ | Ba(6d∥) | 69 ADP$^{22}$ |
| Ba$_8$Al$_{16}$Si$_{30}$ | Ba(6d⊥) | 92 ADP$^{22}$ | Ba$_8$Al$_{16}$Ge$_{30}$ | Ba(6d⊥) | 85 ADP$^{22}$ |
| Ba$_8$Al$_{16}$Si$_{30}$ | Ba(2a) | 111 ADP$^{22}$ | Ba$_8$Al$_{16}$Ge$_{30}$ | Ba(2a) | 101 ADP$^{22}$ |
| Ba$_8$Zn$_{34}$Si$_{39}$ | Ba(6d∥) | 80 ADP$^{22}$ | Ba$_8$Ni$_{46}$Ge$_{40}$ | Ba(6d∥) | 75 ADP$^{22}$ |
| Ba$_8$Zn$_{34}$Si$_{39}$ | Ba(6d⊥) | 90 ADP$^{22}$ | Ba$_8$Ni$_{46}$Ge$_{40}$ | Ba(6d⊥) | 85 ADP$^{22}$ |
| Ba$_8$Ga$_{16}$Si$_{30}$ | Ba(6d∥) | 66 ADP$^{22}$ | Ba$_8$Ni$_{46}$Ge$_{40}$ | Ba(2a) | 103 ADP$^{22}$ |
| Ba$_8$Ga$_{16}$Si$_{30}$ | Ba(6d⊥) | 92 ADP$^{22}$ | Ba$_8$Cu$_6$Ge$_{40}$ | Ba(6d) | 63 ADP$^{22}$ |
| Ba$_8$Ga$_{16}$Si$_{30}$ | Ba(2a) | 112 ADP$^{22}$ | Ba$_8$Cu$_6$Ge$_{40}$ | Ba(6d) | 85 ADP$^{22}$ |
| Ba$_8$Rh$_2$Si$_{43.6}$ | Ba(6d∥) | 99 ADP$^{22}$ | Ba$_8$Cu$_6$Ge$_{40}$ | Ba(2a) | 106 ADP$^{22}$ |
| Ba$_8$Rh$_2$Si$_{43.6}$ | Ba(6d⊥) | 115 ADP$^{22}$ | Ba$_8$Zn$_{34}$Si$_{39}$ | Ba(6d) | 62 ADP$^{22}$ |
| Ba$_8$Ags$_{84}$Si$_{111}$ | Ba(6d∥) | 81 ADP$^{22}$ | Ba$_8$Zn$_{34}$Si$_{39}$ | Ba(6d⊥) | 98 ADP$^{22}$ |
| Ba$_8$Ags$_{84}$Si$_{111}$ | Ba(6d⊥) | 108 ADP$^{22}$ | Ba$_8$Zn$_{34}$Si$_{39}$ | Ba(2a) | 118 ADP$^{22}$ |
| Ba$_8$Ni$_{34}$Si$_{111}$ | Ba(6d∥) | 91 ADP$^{22}$ | Ba$_8$Ga$_{16}$Ge$_{30}$ | Ba(6d) | 60 ADP$^{22}$ |
| Ba$_8$Ni$_{34}$Si$_{111}$ | Ba(6d⊥) | 102 ADP$^{22}$ | Ba$_8$Ga$_{16}$Ge$_{30}$ | Ba(2a) | 108 ADP$^{22}$ |
| Na$_8$Si$_{46}$ | Na(6d∥) | 110 ADP$^{22}$ | Ba$_8$Ga$_{16}$Ge$_{30}$ | Ba(2a) | 108 ADP$^{22}$ |
| Na$_8$Si$_{46}$ | Na(6d⊥) | 147 ADP$^{22}$ | Ba$_8$Rh$_1$Ge$_{42.8}$ | Ba(6d) | 70 ADP$^{22}$ |
| Sr$_8$Al$_{11}$Ge$_{34}$ | Sr(6d∥) | 67 ADP$^{22}$ | Ba$_8$Ag$_6$Ge$_{40}$ | Ba(6d) | 60 ADP$^{22}$ |
| Sr$_8$Al$_{11}$Ge$_{34}$ | Sr(6d⊥) | 125 ADP$^{22}$ | Ba$_8$Ag$_6$Ge$_{40}$ | Ba(6d) | 78 ADP$^{22}$ |
| Sr$_8$Al$_{11}$Si$_{30}$ | Sr(6d∥) | 54 ADP$^{22}$ | Ba$_8$Ag$_6$Ge$_{40}$ | Ba(2a) | 107 ADP$^{22}$ |
| Sr$_8$Al$_{11}$Si$_{30}$ | Sr(6d⊥) | 80 ADP$^{22}$ | Ba$_8$Cd$_{7.2}$Ge$_{38.4}$ | Ba(6d) | 58 ADP$^{22}$ |
| Ba$_8$Ga$_{16}$Sn$_{30}$ | Ba(6d∥) | 67 ADP$^{22}$ | Ba$_8$Cd$_{7.2}$Ge$_{38.4}$ | Ba(6d) | 78 ADP$^{22}$ |
| Ba$_8$Ga$_{16}$Si$_{30}$ | Ba(2a) | 81 ADP$^{22}$ | Ba$_8$In$_{28}$Ge$_{30}$ | Ba(6d) | 65 ADP$^{22}$ |
| K$_8$Ge$_{38}$ | K(6d∥) | 65 ADP$^{22}$ | Ba$_8$I$_{0.2}$Ge$_{43.2}$ | Ba(6d) | 64 ADP$^{22}$ |
| K$_8$Ge$_{38}$ | K(6d⊥) | 97 ADP$^{22}$ | Ba$_8$I$_{0.2}$Ge$_{43.2}$ | Ba(2a) | 85 ADP$^{22}$ |
| K$_8$Ge$_{38}$ | K(2a) | 112 ADP$^{22}$ | Ba$_8$Pt$_{2.7}$Ge$_{41.7}$ | Ba(6d) | 82 ADP$^{22}$ |
| K$_8$Zn$_{44}$ | K(6d∥) | 78 ADP$^{22}$ | Ba$_8$Pt$_{2.7}$Ge$_{41.7}$ | Ba(6d) | 96 ADP$^{22}$ |
| K$_8$Zn$_{44}$ | K(6d⊥) | 97 ADP$^{22}$ | Ba$_8$Au$_6$Ge$_{40}$ | Ba(6d) | 62 ADP$^{22}$ |
| K$_8$Zn$_{44}$ | K(2a) | 120 ADP$^{22}$ | Ba$_8$Au$_6$Ge$_{40}$ | Ba(6d) | 84 ADP$^{22}$ |
| Rb$_8$Sn$_{44}$ | Rb(6d∥) | 54 ADP$^{22}$ | Ba$_8$Au$_6$Ge$_{40}$ | Ba(2a) | 110 ADP$^{22}$ |
| Rb$_8$Sn$_{44}$ | Rb(6d⊥) | 81 ADP$^{22}$ | Sr$_8$Ga$_{16}$Ge$_{30}$ | Sr(6d) | 80 ADP$^{22}$ |
| Rb$_8$Sn$_{44}$ | Rb(2a) | 92 ADP$^{22}$ | Sr$_8$Ga$_{16}$Ge$_{30}$ | Sr(6d) | 104 ADP$^{22}$ |

**Skutterudite**

| compounds | vibration $\omega_E$ (K) | Ref. | compounds | vibration $\omega_E$ (K) | Ref. |
|-----------|--------------------------|-----|-----------|--------------------------|-----|
| NaFe$_2$Sb$_{12}$ | Na | 162 ADP$^{22}$ | CaFe$_2$Sb$_{12}$ | Ca | 114 ADP$^{22}$ |
| SrFe$_2$Sb$_{12}$ | Sr | 113 ADP$^{22}$ | BaFe$_2$Sb$_{12}$ | Ba | 126 ADP$^{22}$ |

**Pyrochlore**

| compounds | vibration $\omega_E$ (K) | Ref. | compounds | vibration $\omega_E$ (K) | Ref. |
|-----------|--------------------------|-----|-----------|--------------------------|-----|
| KO$_2$S$_6$O$_6$ | K | 61 HC$^{22}$ | RbOs$_2$O$_6$ | Rb | 66 HC$^{22}$ |
| CsOs$_2$O$_6$ | Cs | 75 HC$^{22}$ |
FIG. 3: (a) lattice structures of a typical skutterudite and pyrochlore, their cages are shown by green and pink colors, respectively. The closest interspaces between guest and cage atoms are shown for both compounds. (b) The relationship between Fe and $R_{\text{cage}}$ for different vibration modes of guest atoms in skutterudites and pyrochlores. The lines are fitting results by employing exponential functions, and their colors are corresponding to the colors of cages. The data of skutterudite and pyrochlore are derived from Refs. 39, 42. (c) A summary for clathrates, skutterudites and pyrochlores.

TABLE II: Fitting parameters of the relationship between $F_c$ and $R_{\text{cage}}$. $F_c = Ae^{-BR_{\text{cage}}}$.

| vibration modes | A   | B   |
|-----------------|-----|-----|
| clathrate-2a    | 0.28| 3.0 |
| clathrate-6d⊥  | 0.30| 3.0 |
| clathrate-6d∥  | 0.18| 3.0 |
| clathrate-6d∥-ref 18 | 0.15| 3.0 |
| Skutterudite    | 0.32| 4.4 |
| Pyrochlore      | 0.56| 10.6|

for skutterudite and pyrochlore would give rise to a small $R_c$, and it is readily for a cage to be oversized and the guest atom becomes off-centered.

Conclusions

In the present work, we studied the ALE vibration modes of guest atoms in cage materials by focusing on type-I clathrates, skutterudites and pyrochlores. We showed that the 3D van der Waals-type interaction, which is usually important only in molecular solids but negligible in the other types of solids (ionic, covalent, etc.), can be clearly observed in cage compounds with strong covalent framework. The strong covalent bonded cages create a solid wall and chemical pressure between guest atoms and their surrounding frameworks, stabilizing the anomalous low energy phonon modes. In addition to free space and mass parameters, which we derived previously, we introduced another three chemical environment associated factors: (1) coordination number of guest atoms, or the effective number of pairwise potentials; (2) geometry of cages; (3) electronegativity of the component elements of a cage. These five factors work together to determine the interesting soft modes of the rattling vibrations. The 3D van der Waals-type interaction in cage materials should be highly evaluated in the community of superconductivity and thermoelectricity.

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1 A. J. Sievers and S. Takeno. Isotope Shift of a Low-Lying Lattice Resonant Mode. *Phys. Rev.*, 140:A1030–A1032, 1965.
2 A. D. Caplin, G. Grüner, and J. B. Dunlop. Al$_{10}$V: An Einstein Solid. *Phys. Rev. Lett.*, 30:1138–1140, 1973.
3 A. I. Rykov, K. Nomura, T. Mitsui, and M. Seto. Low-energy excitations in brownmillerites and related oxides. *Physica B: Condensed Matter*, 350(4):287–304, 2004. ISSN 0921-4526.
4 B. C. Sales, D. Mandrus, B. C. Chakoumakos, V. Keppens, and J. R. Thompson. Filled skutterudite antimonides: Electron crystals and phonon glasses. *Phys. Rev. B*, 56: 15081–15089, 1997.
5 Z. Hiroi, S. Yonezawa, Y. Nagao, and J. Yamamura. Extremely strong-coupling superconductivity and anomalous lattice properties in the β-pyrochlore oxide KO$_2$O$_6$. *Phys. Rev. B*, 76:014523, 2007.
6 B. C. Sales, B. C. Chakoumakos, R. Jin, J. R. Thompson, and D. Mandrus. Structural, magnetic, thermal, and transport properties of $X_8$Ga$_{16}$Ge$_{30}$ ($X$ = Eu, Sr, Ba) sin-
gle crystals. Phys. Rev. B, 63:245113, 2001.

7. M. Christensen, A. B. Abrahamsen, N. B. Christensen, F. Juranyi, N. H. Andersen, K. Lemmann, J. Andreassen, C. R. H. Bahl, and B. B. Iversen. Avoided crossing of rattler modes in thermoelectric materials. Nature Materials, 7:811–815, 2008.

8. Shoji Yamanaka, Eiji Enishi, Hiroshi Fukuoka, and Masahiro Yasukawa. High-Pressure Synthesis of a New Silicon Clathrate Superconductor, Ba₈Si₃₆. Inorganic Chemistry, 39:56–58, 2000.

9. Jingtao Xu, Jun Tang, Kazumi Sato, Yoichi Tanabe, Hitoshi Miyasaka, Masahiro Yamashita, Satoshi Heguri, and Katsumi Tanigaki. Low-temperature heat capacity of Sr₃Ga₁₆Ge₃₀ and Ba₈Ga₁₆Ge₃₀: Tunneling states and electron-phonon interaction in clathrates. Phys. Rev. B, 82:085206, 2010.

10. Jiuzhen Wu, Jingtao Xu, Dwi Prananto, Hidekazu Shimo-tani, Yoichi Tanabe, Satoshi Heguri, and Katsumi Tanigaki. Systematic studies on anharmonicity of rattling phonons in type-I clathrates by low-temperature heat capacity measurements. Phys. Rev. B, 89:214301, 2014.

11. J. L. Cohn, G. S. Nolas, V. Fessatidis, T. H. Metcalf, and G. A. Slack. Glasslike Heat Conduction in High-Mobility Crystalline Semiconductors. Phys. Rev. Lett., 82:779–782, 1999.

12. Terumasa Tadano, Yoshihiro Gohda, and Shinji Tsuneyuki. Impact of Rattlers on Thermal Conductivity of a Thermoelectric Clathrate: A First-Principles Study. Phys. Rev. Lett., 114:095501, 2015.

13. Tetsuji Kume, Hiroshi Fukuoka, Toshihiro Koda, Shigeo Sasaki, Hiroyasu Shimizu, and Shoji Yamanaka. High-Pressure Raman Study of Ba Doped Silicon Clathrate. Phys. Rev. Lett., 90:155503, 2003.

14. T. Mori, S. Goshima, K. Iwamoto, S. Kushibiki, H. Matsumoto, N. Toyota, K. Suekuni, M. A. Avila, T. Takabatake, T. Hasegawa, N. Ogita, and M. Udagawa. Optical conductivity of rattling phonons in type-I clathrate Ba₈Ga₁₆Ge₃₀. Phys. Rev. B, 79:212301, 2009.

15. Toshiro Takabatake, Koichiro Suekuni, Tsuneyoshi Nakayama, and Eiji Kaneshita. Phonon-glass-electron-crystal thermoelectric clathrates: Experiments and theory. Rev. Mod. Phys., 86:669–716, 2014.

16. K. Suekuni, M. A. Avila, K. Umeo, H. Fukuoka, S. Yamana-ka, T. Nakagawa, and T. Takabatake. Simultaneous structure and carrier tuning of dimorphic clathrate Ba₈Ga₁₆Sn₃₀. Phys. Rev. B, 77:235119, 2008.

17. T. Nakayama and E. Kanashita. Interacting dipoles in typ-I clathrates: Why glass-like though crystalline? EPL (Europhysics Letters), 84(6):66001, 2008.

18. J. Wu, K. Akagi, J. Xu, H. Shimotani, K. K. Huyhn, and K. Tanigaki. Unification of the low-energy excitation peaks in the heat capacity that appears in clathrates. Phys. Rev. B, 93:094303, 2016.

19. M. Christensen and B. B. Iversen. Host Structure Engineering in Thermoelectric Clathrates. Chem. Mater, 19(20):4896–4905, 2007.

20. Simon Johnsen, Anders Bentien, Georg K. H. Madsen, Mats Nygren, and Bo B. Iversen. Crystal structure and transport properties of nickel containing germanium clathrates. Phys. Rev. B, 76:245126, 2007.

21. S. Johnsen, M. Christensen, B. Thomsen, G. K. H. Madsen, and B. B. Iversen. Barium dynamics in noble-metal clathrates. Phys. Rev. B, 82:184303, 2010.

22. M. Christensen and B. B. Iversen. Hostguest coupling in semiconducting Ba₈Zn₃₆Ge₃₈. Journal of Physics: Condensed Matter, 20(10):104244, 2008.

23. Mogens Christensen, Nina Lock, Jacob Overgaard, and Bo B. Iversen. Crystal Structures of Thermoelectric n- and p-type Ba₈Ga₄₆Ge₃₀ Studied by Single Crystal, Multitemperature, Neutron Diffraction, Conventional X-Ray Diffraction and Resonant Synchrotron X-ray Diffraction. Journal of the American Chemical Society, 128(49):15657–15665, 2006.

24. M. Falmbigl, F. Kneidinger, M. Chen, A. Grytsiv, H. Mi-chor, E. Royanian, E. Bauer, H. Effenberger, R. Podloucky, and P. Rogl. Cage-Forming Compounds in the BaRhGe System: From Thermoelectrics to Superconductivity. Inorganic Chemistry, 52(2):931–943, 2013.

25. I. Zeiringer, M. Chen, I. Bednar, E. Royanian, E. Bauer, R. Podloucky, A. Grytsiv, P. Rogl, and H. Effenberger. Phase Equilibria, Crystal Chemistry and Physical Properties of Au-Ba-Ge Clathrates. Acta Materialia, 59:2368–2384, 2011.

26. A. Bentien, E. Nishibori, S. Paschen, and B. B. Iversen. Crystal structures, atomic vibration, and disorder of the type-I thermoelectric clathrates Ba₈Ga₁₆Si₃₀, Ba₈Ga₁₆Ge₃₀, Ba₈In₁₆Ge₃₀, and Sr₃Ga₄₁₆Ge₃₀. Phys. Rev. B, 71:144107, 2005.

27. N. Melnychenko-Koblyuk, A. Grytsiv, P. Rogl, M. Rot-ter, R. Lackner, E. Bauer, L. Fornasari, F. Marabelli, and G. Giester. Structure and physical properties of type-I clathrate solid-solution Ba₈PtₓGe₄₆₋ₓ₋₉Vₙ₋ₓ (V = vacancy). Phys. Rev. B, 76:195124, 2007.

28. Mogens Christensen, Simon Johnsen, and Bo Brummerst-ed Iversen. Thermoelectric clathrates of type I. Dalton Trans., 39:978–992, 2010.

29. N. Nasir, A. Grytsiv, N. Melnychenko-Koblyuk, P. Rogl, E. Bauer, R. Lackner, E. Royanian, G. Giester, and A. Saccone. Clathrates Ba₈(Zn,Cd)₄3₆ₓ₋₇: synthesis, crystal structure and thermoelectric properties. Journal of Physics: Condensed Matter, 21(38):385404, 2009.

30. A. Bentien, B. B. Iversen, J. D. Bryan, G. D. Stucky, A. E. C. Palmqvist, A. J. Schultz, and R. W. Henning. Maximum entropy method analysis of thermal motion and disorder in thermoelectric clathrate Ba₈Ga₄₆Si₃₀. Journal of Applied Physics, 91(9):5694–5699, 2002.

31. M. Falmbigl, A. Grytsiv, P. Rogl, and G. Giester. Clathrate formation in the systems BaIrGe and Ba-(Rh,Ir)-Ge. Crystal chemistry and phase relations. Intermetallics, 36:61–72, 2013.

32. M. Falmbigl, M. X. Chen, A. Grytsiv, P. Rogl, E. Roya-nian, H. Michor, E. Bauer, R. Podloucky, and G. Giester. Type-I clathrate Ba₈Ni₃₆₋ₓ₋₂: Phase relations, crystal chemistry and thermoelectric properties. Dalton Trans., 41:8839–8849, 2012.

33. Sebastian Christensen, Marcos A. Avila, Koichiro Suekuni, Ross Piltz, Toshiro Takabatake, and Mogens Christensen. Combined X-ray and neutron diffraction study of vacancies and disorder in the dimorphic clathrate Ba₈Ga₁₆Sn₃₀ of type I and VIII. Dalton Trans., 42:14766–14775, 2013.

34. T. Tanaka, T. Onimaru, K. Suekuni, S. Mano, H. Fukuoka, S. Yamanaka, and T. Takabatake. Interplay between thermoelectric and structural properties of type-I clathrate K₂Ga₃₆Si₃₀ single crystals. Phys. Rev. B, 81:165110, 2010.

35. S. Stefanoski, J. Martin, and G. S. Nolas. Low temperature transport properties and heat capacity of single-crystal Na₈Si₃₆. J. Phys. Condens. Matter, 22:48504, 2010.

36. J. H. Roudebush, N. Tsujii, A. Hurtando, H. Hope,
Yu. Grin, and S. M. Kauzlarich. Phase Range of the Type-I Clathrate Sr$_8$Al$_x$Si$_{46-x}$ and Crystal Structure of Sr$_8$Al$_{10}$Si$_{36}$. Inorganic Chemistry, 51(7):4161–4169, 2012.

Andreas Kaltzoglou, Thomas Fassler, Mogens Christensen, Simon Johnsen, Bo Iversen, Igor Presniakov, Alexey Sobolev, and Andrei Shevelkov. Effects of the order-disorder phase transition on the physical properties of A$_8$Sn$_{44}$ (A = Rb, Cs). J. Mater. Chem., 18:5630–5637, 2008.

H. Shimizu, Y. Takeuchi, T. Kume, S. Sasaki, K. Kishimoto, N. Ikeda, and T. Koyanagi. Raman spectroscopy of type-I and type-VIII silicon clathrate alloys Sr$_8$Al$_x$Ga$_{16-x}$Si$_{30}$. Journal of Alloys and Compounds, 487(12):47–51, 2009.

W. Schnelle, A. Leithe-Jasper, H. Rosner, R. Cardoso-Gil, R. Gumeniuk, D. Trots, J. A. Mydosh, and Yu. Grin. Magnetic, thermal, and electronic properties of iron-antimony filled skutterudites M$_{1-x}$Fe$_4$Sb$_{12}$ (M = Na, K, Ca, Sr, Ba, La, Yb). Phys. Rev. B, 77:094421, 2008.

J. Xu, J. Wu, H. Shao, S. Heguri, Y. Tanabe, Y. Liu, G. Liu, J. Jiang, H. Jiang, and K. Tanigaki. Structure and thermoelectric properties of the n-type clathrate Ba$_8$Cu$_3$Ge$_{46-x}$Sn$_{0.7}$. Journal of Materials Chemistry A, 3:19100, 2015.

J. Xu, J. Wu, S. Heguri, G. Mu, Y. Tanabe, and K. Tanigaki. Low-temperature physical properties of Ba$_8$Ni$_x$Ge$_{46-x}$ (x = 3, 4, 6). Journal of Electronic Materials, 41(6):1177–1180, 2012.

Zenji Hiroi, Jun-ichi Yamaura, and Kazumasa Hattori. Rattling Good Superconductor: β-Pyrochlore Oxides AO$_2$O$_5$. Journal of the Physical Society of Japan, 81(1):011012, 2012.

I. Zeiringer, E. Bauer, A. Grytsiv, P. Rogl, and H. Effenberger. Phase Equilibria, Crystal Chemistry, and Physical Properties of AgBaSi Clathrates. Jpn. J. Appl. Phys., 50:05FA01, 2011.

J. Xu, J. Wu, S. Heguri, Y. Tanabe, G. Liu, J. Jiang, H. Jiang, and K. Tanigaki. Single Crystal Structure Study of Type I Clathrate K$_8$Zn$_4$Sn$_{42}$ and K$_8$In$_4$Sn$_{38}$. J. Electron. Mater., 46:2765, 2017.

Philip M. Morse. Diatomic Molecules According to the Wave Mechanics. II. Vibrational Levels. Phys. Rev., 34:57–64, 1929.

Manjeera Mantina, Adam C. Chamberlin, Rosendo Valero, Christopher J. Cramer, and Donald G. Truhlar. Consistent van der Waals Radii for the Whole Main Group. The Journal of Physical Chemistry A, 113(19):5806–5812, 2009.

A. Bondi. van der Waals volumes and radii. J. Phys. Chem., 68:441–451, 1964.

M. Koza, L. Capogna, A. Leithe-Jasper, H. Rosner, W. Schnelle, H. Mutka, M. R. Johnson, C. Ritter, and Y. Grin. Vibrational dynamics of filled skutterudites M$_{1-x}$Fe$_4$Sb$_{12}$ (M = Ca, Sr, Ba, and Yb). Phys. Rev. B, 81:174302, 2010.

B. C. Melot, R. Tackett, J. O’Brien, A. L. Hector, G. Lawes, R. Seshadri, and A. P. Ramirez. Large low-temperature specific heat in pyrochlore Bi$_2$Ti$_2$O$_7$. Phys. Rev. B, 79:224111, 2009.

D. P. Shoemaker, R. Seshadri, M. Tachibana, and A. L. Hector. Incoherent Bi off-centering in Bi$_2$Ti$_2$O$_6$′ and Bi$_2$Ru$_2$O$_6$′: Insulator versus metal. Phys. Rev. B, 84:064117, 2011.