

Are type-I clathrates Zintl phases and ‘phonon glasses and electron single crystals’?

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Abstract

We discuss to which extent the concepts of Zintl phases and of ‘phonon glasses and electron single crystals’ apply to type-I clathrates. In (β -) $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ the presence of residual charge carriers appears to be related to a slight off-stoichiometry of the samples pointing to the validity of the Zintl concept in stoichiometric samples. The low and almost stoichiometry independent mobilities of (β -) $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, and $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ seriously question the validity of the ‘electron single crystal’ concept for type-I clathrates. The temperature dependence of the thermal conductivity of a $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ single crystal indicates that tunneling states play a central role in producing ‘phonon glass’-like thermal conductivities.

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1. Introduction

Type-I clathrates are cubic solids made up of large cages of silicon, germanium, or tin (or, in the gas hydrates, of H_2O) which encapsulate ‘guest’ atoms. The cages are face sharing and their constituent atoms tetrahedrally (sp^3 -like) bonded. The bonding situation of these clathrates may, in a first approximation, be understood in terms of the so-called Zintl concept [1]. In a Zintl compound, each constituent attains a closed valence shell by combining a formal charge transfer with covalent

bonds: The more electropositive ‘guest’ atoms donate their valence electrons to the more electronegative ‘host’ (or cage) atoms such that the latter complete their valence requirement (octet rule) and build a covalently bonded cage structure. The ‘guest’ atoms, on the other hand, are weakly ionically bonded to the host framework. Since in this simple concept all valence electrons of type-I clathrates are used in covalent bonds, one would expect them to be semiconductors.

The renewed interest in clathrates (for a review see, e.g. Ref. [2]) derives from the claim [3] that clathrates behave as ‘phonon glasses and electron single crystals (PGEC)’ [4] and, therefore, are promising thermoelectric materials. The ‘guest’

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atoms are believed to undergo large local vibrations ('rattling') in the cages. These 'Einstein modes' may resonantly scatter the heat-carrying acoustic phonons, leading to very low and 'glass-like' thermal conductivities κ , provided that κ is phonon dominated. On the other hand, the residual electronic charge carriers are believed to propagate along the 'host' framework and to be much less affected by the 'rattling' than the heat-carrying phonons. Thus, the ratio of electrical conductivity to thermal conductivity σ/κ should be large, resulting in an enhanced thermoelectric figure of merit, $Z = S^2\sigma/\kappa$, where S denotes the thermoelectric power.

In this contribution we shall critically discuss the validity of the two key concepts addressed above, namely that clathrates are expected to be Zintl compounds and PGECs. As a basis for this discussion we combine our previous results on $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ [5] and literature data of other groups with our new results on $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$.

2. Are clathrates Zintl compounds?

Type-I clathrates of the composition $(\text{II})_8(\text{III})_{16}(\text{IV})_{30}$, where the group III and IV atoms build up the cages and the group II atoms are the 'guests', are generally considered as insulating Zintl compounds, according to the charge-balanced electron count $[(\text{II})^{2+}]_8[(\text{III})^{1-}]_{16}[(\text{IV})^0]_{30}$. Experiments, however, show that most $(\text{II})_8(\text{III})_{16}(\text{IV})_{30}$ clathrates behave metal—rather than semiconductor-like. The question whether this discrepancy is due to a failure of the Zintl concept or due to off-stoichiometry has, to our knowledge, not been answered conclusively. To address this question we have annealed polycrystalline samples of $\beta\text{-Eu}_8\text{Ga}_{16}\text{Ge}_{30}$, prepared as described in Ref. [6], at various temperatures and determined the lattice parameter a as well as several physical properties. As shown in Fig. 1, lowering the annealing temperature T_a leads to an expansion of the unit cell volume $V = a^3$. Recently, a of $\text{Sr}_8\text{Ga}_{16-x}\text{Si}_{30+x}$ was shown to increase with Ga content [7]. Energy dispersive X-ray microanalysis (EDX) gives $x = 0.7(2)$ and

0.57(6) for our $\beta\text{-Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ samples annealed at 680°C and 650°C , respectively, indicating that, also here, the varying Ga content is responsible for the volume change. In Fig. 2 we show the charge-carrier concentration n at 2 K as a function of V . n was determined from the normal part of the Hall coefficient R_H (taking account of the anomalous contribution, cf. Ref. [5]) by using the simple one-band expression $R_H = 1/(ne)$. n varies approximately linearly with V . In the Zintl picture, $x = 1$ creates one conduction electron per formula unit ($x = |n_{\text{per f.u.}}|$). In our samples x would thus vary from 1.5 to 0.4, in good agreement with the EDX results. We conclude

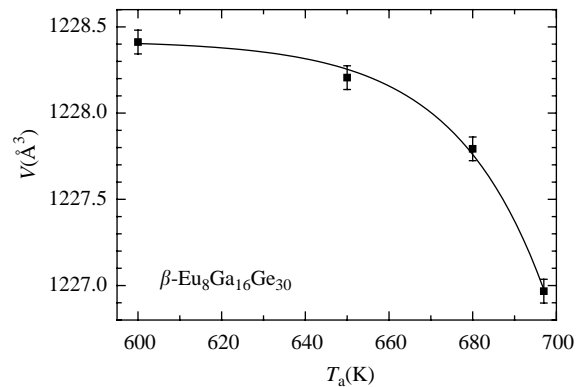


Fig. 1. Unit cell volume V vs. annealing temperature T_a for various $\beta\text{-Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ samples.

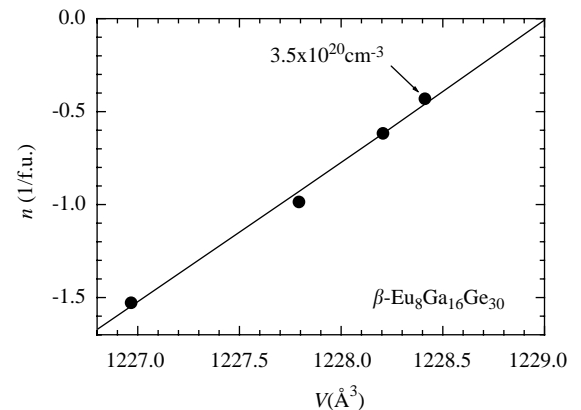


Fig. 2. Charge-carrier concentration n at 2 K vs. unit cell volume V at room temperature of various $\beta\text{-Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ samples annealed at different temperatures.

that the charge carriers observed in β - $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ are due to a slight off-stoichiometry of the samples and that, if the Ga content can be further increased, semiconducting samples will finally become available. Similar studies should be carried out for other clathrates to check for the generality of this statement.

3. Are clathrates ‘electron single crystals’?

To test whether clathrates are ‘electron single crystals’, the charge-carrier mobilities have to be determined. Surprisingly, this has been done only for few Ge based type-I clathrate samples [3,5,8–10]. In Fig. 3 we replot the room temperature Hall mobilities $\mu_{\text{H}} = R_{\text{H}}/\rho$, where ρ is the electrical resistivity, as a function of the room temperature charge-carrier concentrations $n = 1/(R_{\text{H}}e)$ of all these samples. The results of Ref. [3] most probably contain an error in the reported charge-carrier concentrations and had to be omitted. In addition to these literature data we show the data of our β - $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ samples of Figs. 1 and 2. All mobilities range between 3 and 15 cm^2/Vs , which are rather low values. Also the mobilities do, if at all, increase only slightly with decreasing carrier concentration. Thus, samples closer to the exact stoichiometry will, most probably, not have much higher mobilities either. More efforts on the

sample preparation side are necessary to reveal if other defects except for off-stoichiometry are responsible for the low mobilities or whether the mobilities of clathrates are intrinsically low.

4. Are clathrates ‘phonon glasses’?

The ‘rattling’ of the ‘guest’ atoms in clathrates is an intensively discussed topic [2]. Results from several measurement techniques give evidence for this phenomenon. Inelastic neutron scattering experiments on $\text{Na}_8\text{Si}_{46}$ and K_8Si_{46} revealed sharp low-energy peaks in the phonon density of states, which are interpreted as Einstein-like vibrations of Na and K [11]. Also in Raman spectra of $\text{Cs}_8\text{Ga}_{16}\text{Sn}_{30}$ low-frequency vibrational modes have been identified and associated with the ‘rattling’ of the Cs atoms [12]. From structural investigations of clathrates, the so-called atomic displacement parameters (ADPs) of (part of) the ‘guest’ atoms were shown to be strongly enhanced with respect to the other atom positions. However, the temperature dependence of the ADPs indicates [13] that ‘rattling’ is not the only cause of large ADPs. In fact, the large ADPs are usually strongly anisotropic suggesting that the ‘guest’ position should be described by a number of split sites. Then, the ADP of each split site is much reduced. More indirect evidence for the ‘rattling’ comes from measurements of the temperature dependence of the specific heat, which may be well approximated by a Debye and one or two low-energy Einstein terms [5]. While there seems to be some consensus on the presence of ‘rattling’ modes, their influence on the thermal conductivity is still a controversial matter. The situation is complicated by the fact that, unlike in the case of glasses [14], the lattice thermal conductivity κ_{L} of clathrates is far from being universal: Within the class of type-I clathrates [2], $\kappa(T)$ dependencies typical of crystalline solids as well as of amorphous solids are encountered. More dramatically, the same holds true even for samples of the same nominal composition (see, e.g., Refs. [3,8,10,15] for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, Refs. [8,10,16] and Fig. 4 of this work for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, Refs. [5,10,17] for $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$). Obviously, to clarify the situation

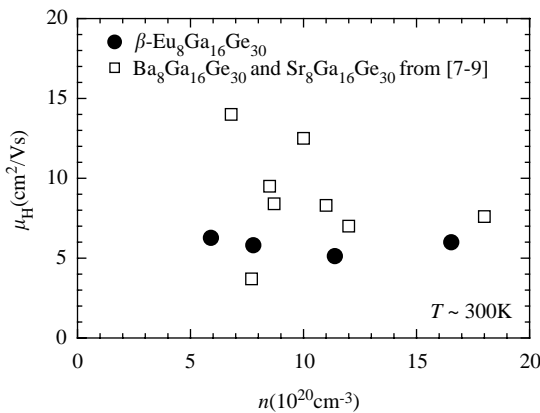


Fig. 3. Hall mobility μ_{H} vs. charge-carrier concentrations n for various β - $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ samples annealed at different temperatures and for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$, and $\text{Eu}_8\text{Ga}_{16}\text{Ge}_{30}$ samples from Refs. [8–10].

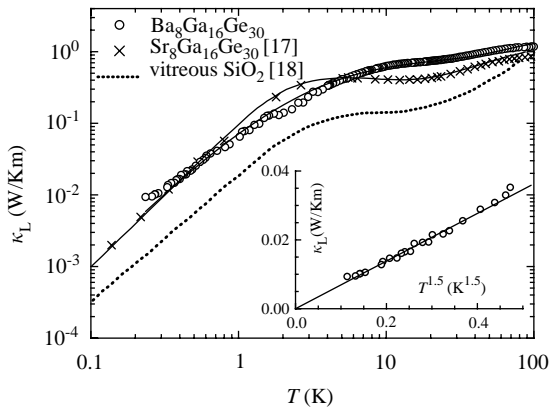


Fig. 4. Temperature dependence of the lattice thermal conductivity $\kappa_L(T)$ of a $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ single crystal. The electronic contribution estimated using the Wiedemann–Franz law is negligibly small in the entire temperature range. For comparison, the $\kappa_L(T)$ data of a $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ polycrystal from Ref. [18] and of vitreous SiO_2 from Ref. [19] are replotted. The solid curves represent best fits to the model discussed in Ref. [18]. The parameters for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ are $A = 12\,000\text{ m}^{-1}\text{ K}^{-1}$, $B = 2.5\text{ K}^{-2}$, $C_1 = 2 \times 10^{27}\text{ m}^{-1}\text{ s}^{-2}\text{ K}^{-2} = C_2/3$, $D = 35\text{ m}^{-1}\text{ K}^{-4}$, $l_{\min} = 4 \times 10^{-10}\text{ m}$, $\theta_D = 355\text{ K}$, $T_{E1} = 121\text{ K}$, $T_{E2} = 72\text{ K}$, and $\gamma_1 = \gamma_2 = 1.5$. The inset shows that $\kappa_L(T) \propto T^{1.5}$ holds for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ below 0.6 K.

the reasons for these big differences have to be found. Are the low thermal conductivities observed in some samples intrinsic? How big is the role of structural disorder and grain boundaries? Also, $\kappa(T)$ measurements should be extended to lower temperatures where the identification of the dominant scattering mechanism may be easier. This has, so far, been done only for a $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ polycrystal [18]. Here, we present results of $\kappa(T)$ measurements down to 300 mK on a $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ single crystal prepared by zone melting. In Fig. 4 we compare them to the data on $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ from Ref. [18] and on vitreous SiO_2 from Ref. [19]. The overall behaviour is quite similar for all three materials justifying, to some extent, the use of the terminus ‘phonon glass’ for these $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ samples. However, Slack’s original definition of a ‘phonon glass’ [4] was a system which possesses the theoretical minimum thermal conductivity κ_{\min} . As already shown in Ref. [18], $\kappa_L(T)$ of $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ is three orders of magnitude larger than κ_{\min} at 1 K and approaches κ_{\min} only at room temperature. The same is true for

$\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$. Below 1 K, $\kappa(T)$ of vitreous SiO_2 varies as T^n with $n \approx 1.8$, the exponent typically observed for many non-crystalline solids and associated with the phonon scattering from tunneling states [19]. The exponent for our $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ sample is 1.5, as shown in the inset of Fig. 4, while a value of 2 was given for $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ in Ref. [18]. Also the plateau in $\kappa(T)$, characteristic of non-crystalline solids, is observed for both clathrate samples. An attempt to identify the dominant scattering mechanisms in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ was made in Ref. [18]: $\kappa_L(T)$ was modelled (cf. fit in Fig. 4) using the kinetic gas-theory expression $\kappa_L = (v/3) \int_0^{\omega_D} C(\omega)l(\omega) d\omega$ with a Debye specific heat C and a phonon mean free path l due to tunneling states, resonant scattering, and Rayleigh scattering. The resonant scattering term captures the scattering of the acoustic phonons from the ‘rattle’ modes. The tunneling states may be associated with ‘guest’ atoms tunneling between different split sites. Using the same procedure as in Ref. [5] we obtain the fit for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ shown in Fig. 4. For the obtained fit parameters (cf. caption of Fig. 4), scattering from tunneling states is the dominating scattering mechanism in almost the entire temperature range. Indeed, it has been shown that one of the two different ‘guest’ sites in both $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$ and $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ should be described by split sites [5,18]. Independent evidence for the presence of tunneling states in $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ comes from ultrasound attenuation measurements where the T^3 dependence typical for structural glasses was observed [16]. Thus, for obtaining the low (‘glassy’) thermal conductivities observed for some clathrates, the presence of split sites may be more important than the much discussed ‘rattling’.

Acknowledgements

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