Electronic structure and transport in type-I and type-VIII clathrates containing strontium, barium, and europium

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The thermoelectric properties of filled gallium-germanium clathrates are analyzed from a band-structure point of view. Using the virtual crystal approximation the undoped clathrates are calculated to be semiconductors with band gaps around 0.6-0.9 eV. The conduction bands hybridize with the unoccupied *d* states of the guest atoms. This means that the thermoelectric properties of *n*-doped type-I clathrates depend strongly on the guest atom while *p* doped clathrates are relatively unaffected. The type-VIII structures have disperse bands centered around the voids in the framework structure. This explains the low effective masses observed for *n*-doped type-VIII structures. It also means that the electronic structure and thermoelectric properties are relatively independent of the guest atom and that *p*-doped should have favorable thermoelectric properties while *n*-doped type-VIII structures have poor properties. We estimate a figure of merit of 1.2 at 400 K for an optimally *p*-doped europium-VIII clathrate. In addition we predict that the strontium-VIII clathrate should be stable.

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I. INTRODUCTION

Clathrates are open framework structures containing guest atoms in their cages. They have recently received much attention because of their potential use in thermoelectric devices. The interest in the clathrates comes from the suggestion that they can act as phonon glass electron crystals (PGECs).¹ The concept of a PGEC is based on the assumption that the heavy guest atoms rattle inside the cages, thereby scattering phonons without reducing the framework conductivity. The advantage of a high electrical conductivity σ and a low the thermal conductivity (electronic and lattice) κ is seen immediately from the definition of the dimensionless figure of merit $ZT = (\sigma T/\kappa)S^2$. ZT gives the performance of a given thermoelectric material which should thus also have a high Seebeck coefficient S. This is because the electronic part of the thermal conductivity according to the Wiedemann-Franz relation is proportional to σT , thus limiting the value of ZT that can be obtained for a given S. Type-I clathrates with the composition $X_8Y_{16+x}Z_{30-x}$ (where X is a divalent cation and Y and Z are group-III and group-IV elements, respectively) have been known for a long time.² The compounds with the ideal Zintl stoichiometry (x=0) can be expected to be semiconductors and thereby to have reasonably high Seebeck coefficients close to the band edges. Consequently much attention has focused on this composition and the first experimental confirmation^{3,4} of the PGEC concept in clathrates was based on type-I clathrates with Ga-Ge frameworks containing Sr or Eu guest atoms (in the following named SrGaGe-I and EuGaGe-I). In this pioneering work high Seebeck coefficients and electron mobilities, together with lattice thermal conductivities typical for amorphous materials, were found.^{3,4} Since then several type-I Ga-Ge clathrates have been made and their transport properties characterized.⁵⁻⁸ All these studies report quite different properties depending not only on the compound composition but also on the way the sample was prepared.

The present study was prompted by recent results on the Eu clathrates, which have a special interest because of the magnetic guest atom. While some authors found good electron mobilities,⁴ others found low electron mobilities^{6,7} leading one group to question the concept of an electron crystal.⁷ Furthermore a new type-VIII clathrate with the same $Eu_8Ga_{16}Ge_{30}$ unit-cell composition was reported and characterized. ^7 Like an earlier study of $BaGaSn\text{-VIII}^5$ the type-VIII clathrate had a higher resistivity and Seebeck coefficient compared to the type-I clathrates.⁷ This is somewhat surprising because low band masses were found for the conduction bands of the type-VIII structure,⁵ but consistent with the low carrier concentrations found in the two studies.^{5,7} The low band masses of the type-VIII structure should mean that it is not a promising candidate for thermoelectric applications, and it is interesting to find out whether this property is intrinsic of the type-VIII clathrate or depends on the doping level and guest-atoms.

To understand the influence of crystal structure, doping, and magnetism on the thermoelectric properties we report band-structure calculations and analyze them using semiclassic transport theory.⁹ This method has previously been successfully applied to several thermoelectric materials,^{10–14} and the formalism has been described in detail in these papers. It has already been applied to SrGaGe-I and BaGaGe-I.¹⁴ We will also discuss these two compounds, both because it makes the understanding of the EuGaGe-I and the type-VIII clathrates easier and because we disagree with some of the interpretations of the former study.¹⁴

II. COMPUTATIONAL DETAILS

The calculations were performed using the L/APW+lo method^{15,16} as implemented in the WIEN2K code.¹⁷ Sphere

sizes of 2.28 and 2.6 a.u. were used for the framework and guest atoms, respectively. The plane-wave (PW) cutoff was defined by $\min(R_{MT})\max(k_n)=6.2$ corresponding to approximately 3700 PW for the type-I clathrates and 1900 PW for the type-VIII clathrates. The Brillouin zone (BZ) was sampled on a tetrahedral mesh with 1200 k points (35 in the IBZ) for the type-I clathrates and 2400 (84 in the IBZ) for the type-VIII clathrates. Geometry optimization and total energy calculations were done with the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) (Ref. 18) within density functional theory (DFT). It is well known that most DFT-based functionals yield band gaps that are smaller than experiment by approximately 50%. Therefore band structure calculations were performed using the Engel-Vosko (EV) GGA.¹⁹ The EV-GGA has been designed by optimizing the virial relation instead of E_{ex} and thus the related energy bands are known to be closer to experiment.^{20,21} An on-site U term of 10 eV (Ref. 22) was added within the local density approximation (LDA)+Umethod^{23,24} to treat the strongly correlated 4f electrons on Eu. For the transport calculations eigen-energies were calculated for 6000 k points (165 in the IBZ) for the type-I clathrates and 12000 k points (322 in the IBZ) for the type-VIII clathrates. An analytical expression of the bands was obtained by a smoothed Fourier interpolation²⁵ of the bandenergies. The necessary derivatives were then calculated on a FFT grid three times as dence in all direction using the Fourier coefficients.

Structural model

A detailed discussions of the type-I and -VIII clathrate framework structures was given in Ref. 7. The type-I framework is built from two cage types, the smaller pentagonal dodecahedra which has 20 vertices and the larger tetrakaidecahedron built from 24 vertices. Several experiments have shown that the guest-atoms inside the large cages of the type-I structures are disordered around the 6*d* (center of the cage) positions.^{6,7,26–28} To check the influence of the guestatom position we have performed test calculations for SrGaGe-I displacing the Sr atoms from the 6*d* positions. We found only a small lowering of the energy and little influence on the calculated band structure. Therefore all electronicstructure calculations were performed with the guest-atoms placed on their average high-symmetry positions.

The framework atoms (Ga and Ge in the present case) are placed on three crystallographic inequivalent positions. Since Ga and Ge can hardly be distinguished by x-rays, it is difficult to determine whether they preferentially order on the crystallographic inequivalent sites. By integrating the electron density obtained from x-ray diffraction it has been found that Ga preferentially occupies the 6c site and avoids the 16isite.²⁹ This was confirmed by a resonant x-ray diffraction study³⁰ where 76%, 24%, and 43% Ga were found on the 6c, 16i, and 24k sites, respectively. A conflicting result has been obtained by neutron diffraction on single crystal Sr/Ba/ EuGaGe-I clathrates^{26,27} where no preferential ordering was found. To shed some light on the framework occupancies, we have constructed two virtual crystal (VC) models, one using a fractional nuclear charge of 31.65 corresponding to a

TABLE I. Calculated and experimental (Refs. 2, 5, 7, 26, 27, and 31) cell axes in Å. When several measurements of the unit cell are published the average value and standard deviation are used as the experimental values. Energy differences at the optimized volumes between the type-I and type-VIII clathrates, ΔE_{I-VIII} , are in mRy.

Guest	a _{calc} -I	a _{exp} -I	a _{calc} -VIII	a _{exp} -VIII	ΔE_{I-VIII}
Sr	10.847	10.720(18)	10.776	-	16.3
Ba	10.917	10.767(21)	10.854	-	-38.6
Eu	10.830	10.706	10.756	10.628	23.3

Ga/Ge ratio of 16/30 on each framework site (VC1) and one using fractional nuclear charges of 31.27, 31.84 and 31.62 corresponding to the above mentioned occupancies found by resonant diffraction (VC2).³⁰ We then calculated the forces on the atoms in the two experimental structures^{26,30} and found that they, especially on the 16*i* site, are smaller by approximately a factor 4 when using the VC2 model. This supports the interpretation that Ga avoid the 16i site due to the short bond between the 16i sites in the type-I clathrates.^{7,31} We conclude that the VC2 model based on the preferential occupation³⁰ is the most probable, and perform our electronic structure calculations in this model. However, due to the limited reliability of the total energy using VC models, we have performed the calculations of relative stabilities, discussed in Sec. III, in the VC1 model, which can be kept the same for different structure types.

The framework of the type-VIII clathrate is built from distorted pentagonal dodecahedra containing 23 vertices instead of 20. As opposed to the type-I structure the packing of the cages is not space filling and small voids consisting of eight framework atoms are formed.⁷ As no information is available about preferential occupation in the framework, all calculations will be performed in the VC1 model. This also seems reasonable as there are no unusual short bonds in the framework.

III. RESULTS AND DISCUSSION

A. Structures and relative stabilities of type-I and type-VIII clathrates

To the best of our knowledge SrGaGe-VIII and BaGaGe-VIII have not been prepared so far. To compare their relative stabilities we have fully geometry optimized Sr, Ba, and Eu containing type-I and -VIII clathrates in the VC1 model (Table I). It can be seen that the unit-cell constants are overestimated by 1-2% which is common using the GGA. Still the differences in size of the unit cells are in good agreement with experiment where available. The Ba containing clathrates are significantly larger than those containing Sr and Eu, in accordance with the expectation that Ba²⁺ is a larger cation than Sr²⁺ and Eu²⁺.

Table I shows that SrGaGe-VIII and EuGaGe-VIII have a lower energy than their type-I analog by approximately 20 mRy, while for Ba the type-I structure is more stable. It is therefore not surprising that EuGaGe melts incongruently

and we predict that SrGaGe under the right conditions will probably do the same. It is quite surprising that the Sr and Eu type-VIII clathrates are lower in energy than the type-I since experimentally only EuGaGe-VIII has been made so far and the type-I clathrates are obtained in much higher yields. However Table I is a qualitative guide. It is not directly related to the full phase diagram for several reasons. First of all we have placed the guest ions in the large cages of the type-I structure on their average positions, though this is probably not a severe limitation. When displacing the Sr guests in SrGaGe-I we found an energy lowering of only ~ 1 mRy. Second, the phonon spectrum of the type-I and -VIII structures can be expected to be quite different due to the different cage sizes, so their relative stabilities will depend on the temperature at which the clathrates are grown. Furthermore the relative stability will depend on the doping level, which, as will be discussed in Sec. IIIB, strongly influences the bonding between the guest-atoms and the framework. Finally, the VC model of disorder is limited with respect to total energies.³² When the same average occupation factors are used, as assumed here, the total energies can be compared between two different structures, but one can easily imagine that one of the systems could lower its energy by a preferred occupation, as is also indicated by some experiments.³⁰

Still the prediction that SrGaGe-VIII should be more stable seems reasonable considering that Eu^{2+} has an ionic radius similar to Sr^{2+} . Ba^{2+} is larger, and thus the type-I structure with the larger tetrakaidecahedral cages is preferred. This is in accord with the fact that the Sn-analogue, BaGaSn-VIII, which has a significantly larger unit cell volume, can be prepared.⁵

B. Electronic structure

1. Type-I clathrates

The density of states (DOS) of SrGaGe-I and BaGaGe-I are shown in Fig. 1. In agreement with earlier¹⁴ findings, the conduction bands are influenced by the guest atoms whereas the valence bands are not much affected. Previously the differences in the conduction bands of SrGaGe-I and BaGaGe-I have been explained as a structural effect, because the Sr in the large cages move further away from the center than the Ba atoms.¹⁴ This cannot be the proper explanation since we have fixed the guest atoms at the centers of the cages. Instead Figs. 1(b) and 1(c) show a strong hybridization between the unoccupied *d* states of the guest atoms and the antibonding framework states. In our opinion this hybridization explains the difference in the conduction bands which is caused by the larger radial extension of the Ba *d* states with respect to Sr.

Figure 2(a) shows the DOS of EuGaGe-I. There is only a small exchange splitting of the valence bands ($\sim 0.05 \text{ eV}$) whereas a strong and opposite splitting ($\sim 0.35 \text{ eV}$) of the conduction bands occurs. The small exchange splitting of the valence bands can be explained by the Eu 4*f* states being too localized to overlap directly with the framework orbitals. However, they induce a strong exchange splitting of the unoccupied Eu 5*d* states which hybridize with, and induce an exchange splitting of, the conduction bands. An analysis of



FIG. 1. (a) DOS in the SrGaGe-I and BaGaGe-I clathrates. Total DOS. Full line: SrGaGe-I. Broken line: BaGaGe-I. (b) and (c) Projected DOS. Full line: Total DOS per atom. Broken line: total *d*-DOS per atom of guest in small cage. Dotted line: total *d*-DOS/ atom of chalkogenide in a large cage.

the partial DOS confirms that also in EuGaGe-I there is a strong contribution from the unoccupied *d* states to the conduction bands. Apart from the exchange splitting, the DOS of EuGaGe-I [Fig. 2(a)] is surprisingly similar to SrGaGe-I [Fig. 1(a)]. If, as we assume, the hybridization with the unoccupied *d* states on the guest-atoms is responsible for the shape of the conduction band DOS, the 5*d* radial behavior of Eu^{2+} must be similar to the 4*d* of Sr²⁺. Indeed Fig. 2(b) shows that the unoccupied 5*d* orbital of Eu²⁺ is much more contracted than the 5*d* of Ba²⁺ and very similar to the 4*d* of Sr²⁺. This can be attributed to the higher nuclear charge of Eu, which leads to a contraction of the orbitals compensating the effect of the expansion when going from 4*d* to 5*d* states.

Table II gives the calculated band gaps. It can be seen that, apart from the spin splitting, SrGaGe-I and EuGaGe-I have similar band gaps while BaGaGe-I has a larger band gap. This can be explained by Ba being more electropositive, thereby stabilizing the bonding sp^3 framework states with respect to the antibonding, which will increase E_{g} .³³ To confirm this interpretation we have performed calculations on a hypothetical Zintl clathrate labeled
GaGe-I (Table II). This model clathrate has empty cages and instead two extra electrons per removed cation were added to the framework. The cell was kept neutral by adding a compensating positive background charge. As expected, this "perfect cation" Zintl clathrate has an even larger band-gap of 1.45eV. Our theoretical band gaps (Table II) are somewhat larger than what was found in earlier calculations (approximately 0.5 eV for BaGaGe-I and 0.3 eV for SrGaGe-I).¹⁴ We attribute this increase to the use of the EV-GGA (we found band gaps similar to those published earlier when using the PBE-GGA). No direct measurements of E_g in type-I GaGe clathrates have been reported. Taking into account the well known underestimation of E_g with standard GGA functionals and the experience with the EV-GGA potential²⁰ we believe our band gaps (Table II) to be more reliable. It should be pointed out



FIG. 2. (a) DOS in the EuGaGe-I clathrate. For illustration the position of the Fermi level for $x = \pm 1$ is marked by broken lines. (b) Calculated radial probability function p(r)=R(r)r of the first unoccupied *d*-state in the free cations: Sr^{2+} (full line), Ba^{2+} (broken line), and Eu^{2+} (dotted line).

that the band gaps are little affected by the VC model used and are calculated approximately 0.1 eV smaller using VC1.

2. Type-VIII clathrates

Figure 3(a) shows the DOS of the type-VIII clathrates, which exhibits similarities to the type-I DOS (Figs. 1 and 2).

TABLE II. Band gaps (in eV) of type-I and type-VIII clathrates. Calculated using VC2 (see the text).

Clathrate	E_g (eV)
Sr-I	0.71
Ba-I	0.89
Eu-I	0.48(↑)/0.77(↓)
□-I	1.45
Sr-VIII	0.56
Ba-VIII	0.88
Eu-VIII	$0.37(\uparrow)/0.73(\downarrow)$



FIG. 3. (a) DOS for SrGaGe-VIII (full line), BaGaGe-VIII (broken line), and EuGaGe-VIII (dotted line). (b) Band structure for the spin- \uparrow states in EuGeGe-VIII. The size of the spheres correspond to the contribution from the Eu guest atom.

The band gaps in the type-VIII clathrates show a similar trend as to those type-I clathrates, confirming that E_g is mainly determined by how electro-positive the dopant atom is. Furthermore in EuGaGe-VIII a large exchange splitting of the conduction bands is found but only a small splitting in the valence bands.

Compared to the type-I clathrates it is surprising that the DOSs from the lowest conduction bands do not depend on the guest atom. Figure 3(a) shows that the DOS in this region is mainly determined by one relatively dispersive framework band that has a minimum in energy close to the H point $(2\pi/a(1.0.0))$ where it hybridizes very little with the guest atoms. Figure 4(a) shows the electron density from just the lowest conduction state at the H point in the BZ. This state is mainly centered around the small voids, and the independence of the DOS on the guest atom is thus due to the nonspace-filling character of the distorted pentagonal dodecahedra and can thus be expected to be inherent to the type-VIII clathrate structure. This explains the low band masses observed for the *n*-doped type-VIII structures.^{5,7} What is also interesting to note about Fig 3(b) is the presence of relatively disperse parabolic valence bands close to the Fermi level. In Fig 4(b) we plot the density from the highest occupied state at the Γ point. Again it is seen that this state is centered around the framework voids. These observations explain the experimentally observed low effective mass, as inherent to the type-VIII framework structure and predict it to be relatively independent of doping and guest-atoms.

C. Transport properties

1. Type-I clathrates

The calculated transport coefficients at 300 K are shown in Figs. 5 and 6. If τ is independent of band energy, both the Seebeck coefficients *S* and the Hall coefficients R_H are independent of the scattering time. By comparing the calculated coefficients with the experimentally measured, one can obtain an estimate of the doping of a prepared sample. Under the assumption that τ and κ are independent of the doping level the electronic power factor relative to the scattering time, $S^2 \sigma / \tau$ [Figs. 5(c) and 6(c)] is proportional to *ZT*.



FIG. 4. Calculated electron density in SrGaGe-VIII from (a) the lowest conduction state at the *H* point. The surface covers a volume where the electron density is larger than $0.03e/Å^3$. The state is threefold degenerate and (b) the highest valence state at the Γ point. The surface covers a volume where the electron density is larger than $0.02e/Å^3$.

Figure 5(a) shows that the Seebeck coefficient for *n*-doped BaGaGe-I is lower than for SrGaGe-I. This results in a significant decrease of $S^2 \sigma / \tau$, Fig. 5(c). As was expected from the DOS analysis, the calculated transport properties for EuGaGe-I are similar to SrGaGe-I (Fig. 5). As is also expected the *p*-doped type-I clathrates show much less dependency on the guest-atom and when optimally *p*-doped all type-I clathrates have a higher $S^2 \sigma / \tau$ than the optimally *n*-doped clathrates.

There are several notable differences between the type-I and -VIII clathrates (Fig. 6). As a result of the conduction band with the low effective mass the Seebeck coefficient and the conduction are low for the *n*-doped type-VIII clathrates. This results in poor thermoelectric properties [Fig. 6(c)]. On the other hand *p*-doped type-VIII clathrates have high Seebeck coefficients close to the band edges *together* with reasonable conduction. This is a result of the copresence of the parabolic like bands centered around the voids (Fig. 4), and the usual quite heavy mass covalent framework bands. Con-



FIG. 5. Transport properties of type-I clathrates at 300 K as a function of doping *x* (e/unitcell). (a) absolute Seebeck coefficient, |S|, (b) conductivity relative to scattering time, σ/τ , and (c) power factor with respect to scattering time $S^2\sigma/\tau$ as a function of doping. SrGaGe-I (full line), BaGaGe-I (broken line), and EuGaGe-I (dotted line). The experimentally investigated carrier range is marked by a bar in the bottom right plot.



FIG. 6. Transport properties of type-VIII clathrates at 300 K as a function of doping x (e/unitcell). (a) absolute Seebeck coefficient, |S|, (b) conductivity relative to scattering time, σ/τ , and (c) power factor with respect to scattering time $S^2\sigma/\tau$ as a function of doping. SrGaGe-VIII (full line), BaGaGe-VIII (broken line), and EuGaGe-VIII (dotted line). The experimentally investigated carrier range is marked by a bar in the bottom right plot.

TABLE III. Doping levels x (e/unitcell) estimated by comparing calculated and experimental Seebeck and Hall coefficients. The R_H values reported for 2 K have been corrected for anomalous contributions (Refs. 7 and 34).

	Experimental	<i>x</i> e/u.c.
EuGaGe-I		
Ref. 4	$S(300 \text{ K}) = -152 \ \mu \text{V/K}$	-0.15
Ref. 6	$S(300 \text{ K}) = -48 \ \mu \text{V/K}$	-1.25
Ref. 7	$S(300 \text{ K}) = -64 \ \mu \text{V/K}$	-0.98
	$1/R_H(2 \text{ K}) = -1.5e/\text{u.c.}$	-0.94
Ref. 34	$S(300 \text{ K}) = -165 \ \mu \text{V/K}$	-0.12
$\beta - 1$ sample	$1/R_H(2 \text{ K}) = -0.4e/\text{u.c.}$	-0.25
EuGaGe-VIII		
Ref. 7	$S(300 \text{ K}) = -71 \ \mu \text{V/K}$	-0.27
	$1/R_H(2 \text{ K}) = -0.46e/\text{u.c.}$	-0.25
Ref. 34	$S(300 \text{ K}) = -160 \ \mu \text{V/K}$	-0.027
$\alpha - 4$ sample	$1/R_H(2 \text{ K}) = -0.14e/\text{u.c.}$	-0.023

sequently good thermoelectric properties [Fig 6(c)] are calculated.

For a comparison with experiment, we have also calculated Hall coefficients, R_H . $1/R_H$ is typically interpreted as the number of carriers in experimental studies, which is valid in a parabolic one-band model. We do find an linear relationship between $1/R_H$ and x (SrGaGe-I: $x \approx 0.66/R_H$; BaGaGe-I: $x \approx 1.0/R_H$; EuGaGe-I: $x \approx 0.65/R_H$) for the conduction bands, but only an approximate one to one correspondence for BaGaGe-I. The valence bands of the type-I clathrates show a significant deviation from a parabolic behavior, and the relation between x and $1/R_H$ is closer to being exponential. For type-VIII conduction bands one also finds an almost linear relation (SrGaGe-VIII: $x \approx 0.63/R_H$; BaGaGe-VIII: $x \approx 0.59/R_H$; EuGaGe-I: $x \approx 0.59/R_H$), which, as expected, is quite independent of the guest atom.

As mentioned above one can use S and R_H to estimate the experimental doping (Table III). This analysis shows the EuGaGe-I samples of Refs. 6 and 7 had high n-carrier concentrations and were far from optimally doped while the sample by Cohn *et al.*⁴ was very close to be optimally ndoped, which explains the differences observed. Furthermore, during the preparation of this paper, a very interesting experimental work was brought to our attention.³⁴ Here the n-type carrier concentration in EuGaGe-I and EuGaGe-VIII is varied systematically by controlling the annealing temperature.³⁴ Table III shows a comparison with the most promising samples from this study. As shown in Table III the EuGaGe-I sample is close to being optimally *n* doped. Therefore only a small improvement to the measured ZT=0.4 at 400 K can be achieved by working on the *n* doping, whereas an improvement of approximately 30% could be achieved if optimally p doped.

For EuGaGe-VIII ZT=0.3 has been achieved experimentally,³⁴ but not much was improved by varying the *n*-doping level. This is also what one would expect from our results [Fig. 6(c)] and can be explained by the lack of high mass states in the conduction bands, discussed in Sec. III A. Nevertheless an improvement by almost a factor four should be possible if an optimal *p*-doping can be achieved, which gives an estimate of ZT=1.2 at 400 K at optimal doping.

An estimated ZT=1.2 at 400 K would make p-doped EuGaGe-VIII a very interesting compound. It should be pointed out that this value is based on two assumptions, namely, that τ and κ are independent of doping level. With respect to τ , it is remarked that there is a good agreement between the doping levels estimated from the Hall coefficient and the Seebeck coefficient for EuGaGe-VIII (Table III) which lends credibility to our approach. Furthermore it is noted that with the substantial exchange splitting of the conduction bands one would expect a magnetic scattering contribution to τ . This is also seen experimentally by a rapid drop in resistivity below the magnetic ordering temperature.^{6,7,34} The exchange splitting of the valence bands is substantially lower than that of the conduction bands; therefore one could expect τ to be larger for *p*-doped samples thus further improving the ZT. The independence of κ is certainly not completely justified. However, as expected from the Wiedemann-Franz relation, the experimental trend is towards lower thermal conductivity with lower doping.³⁴ The calculated optimal p doping is at a very low carrier concentration which, together with the larger expected τ for the valence bands, make it reasonable to expect that the estimate of ZT = 1.2 at 400 K could actually be on the conservative side. Earlier a ZT = 1.7 has been estimated for type-I clathrates at 800 K.14 At this temperature no experimental data are available and the extrapolation was based on the highly improbable assumption that τ is independent of temperature.

IV. CONCLUSIONS

We have calculated the band-structure of Sr, Ba, and Eu containing type-I and -VIII clathrates, and found them to be semiconductors with band gaps around 0.6–0.9 eV. The conduction bands hybridize with the unoccupied *d* states of the guest atoms which means that the conduction bands are similar for the Eu- and Sr-containing clathrates. The unoccupied Ba^{2+} states are more diffuse which results in a different shape of the conduction bands in BaGaGe-I and a lower $S^2\sigma/\tau$.

Comparisons with recently published experimental results have led to several interesting insights. The low band masses observed for the type-VIII clathrates have been explained by the voids in the framework structure. Also the relative independence on the *n*-carrier concentration of the thermoelectric properties of EuGaGe-VIII have been explained. We have also predicted that the thermoelectric properties of the type-VIII clathrate should be relatively independent of the guest atom and that the SrGaGe-VIII clathrate should be stable. Though the Sr containing clathrate is expected to have a higher thermal conductivity the good electronic properties of *p*-doped SrGaGe-VIII could make it interesting for application simply because Sr is much cheaper than Eu.

The current study also emphasizes that, when looking for new thermoelectric materials in compounds as chemically rich as the clathrates, band structure calculations can be a good tool, not only to rationalize experimental results, but also to point out interesting new directions for experiments. The present study has especially underlined the interesting features of the type-VIII clathrates. First of all the performance of *n*-doped EuGaGe-VIII and its relative independence to the amount of *n* doping could naturally have led to the conclusion that the type-VIII structure is not interesting. We estimate ZT = 1.2 at 400 K at optimal *p* doping. Although making *p*-doped samples could be difficult,³⁴ they have been

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- ¹G. Slack, in *CRC Handbook of Thermoelectrics*, edited by D. M. Rowe (CRC, Boca Raton, FL, 1995), pp. 407–440.
- ²B. Eisenmann, H. Schäfer, and R. Zagler, J. Less-Common Met. 118, 43 (1986).
- ³G.S. Nolas, J.L. Cohn, G.A. Slack, and S.B. Schujman, Appl. Phys. Lett. **73**, 178 (1998).
- ⁴J.L. Cohn, G.S. Nolas, V. Fessatidis, T.H. Metcalf, and G.A. Slack, Phys. Rev. Lett. 82, 779 (1999).
- ⁵V.L. Kuznetsov, L.A. Kuznetsova, A.E. Kaliazin, and D.M. Rowe, J. Appl. Phys. 87, 7871 (2000).
- ⁶B.C. Sales, B.C. Chakoumakos, R. Jin, J.R. Thompson, and D. Mandrus, Phys. Rev. B 63, 245113 (2001).
- ⁷S. Paschen, W. Carrillo-Cabrera, A. Bentien, V.H. Tran, M. Baenitz, Y. Grin, and F. Steglich, Phys. Rev. B 64, 214404 (2001).
- ⁸J.D. Bryan, N.P. Blake, H. Metiu, B.B. Iversen, R.D. Poulsen, and A. Bentien, J. Appl. Phys. **92**, 7281 (2002).
- ⁹J. M. Ziman, *Electrons and Phonons* (Clarendon, Oxford, 2001).
- ¹⁰D.J. Singh and I.I. Mazin, Phys. Rev. B 56, 1650 (1997).
- ¹¹M. Fornari and D.J. Singh, Phys. Rev. B **59**, 9722 (1999).
- ¹²R.W. Nunes, I.I. Mazin, and D.J. Singh, Phys. Rev. B 59, 7969 (1999).
- ¹³S.-G. Kim, I.I. Mazin, and D.J. Singh, Phys. Rev. B 57, 6199 (1998).
- ¹⁴N.P. Blake, S. Latturner, J.D. Bryan, G.D. Stucky, and H. Metiu, J. Chem. Phys. **115**, 8060 (2001).
- ¹⁵E. Sjöstedt, L. Nordström, and D.J. Singh, Solid State Commun. **114**, 15 (2000).
- ¹⁶G.K.H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nordström, Phys. Rev. B 64, 195134 (2001).
- ¹⁷P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties. ISBN 3-9501031-1-2, Vienna University of Technology, Austria, 2001.
- ¹⁸J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
- ¹⁹E. Engel and S.H. Vosko, Phys. Rev. B **47**, 13 164 (1993).
- ²⁰P. Blaha (unpublished). The EV-GGA was tested for a number of narrow-band gap semiconductor and the calculated band gaps (for examples 1.23 eV for Si, 0.39 eV for Ge, 1.04 eV for GaAs,

made of BaGaGe-I (Ref. 35) and the experimental control is improving rapidly at the moment. Furthermore the type-VIII clathrate could also be interesting if the framework can, for example, be doped with, i.e., transition metal atoms.³⁶ This could induce heavy-effective-mass bands close to the low mass conduction band in the proximity of E_F and thus lead to an electronic structure favorable for good thermoelectric performance.

and 0.23 eV for InSb) compares much better with the experiment than the PBE-GGA. They also compare very well, and in several cases better, with experiment than more elaborate, and in principle theoretically more justified, approaches based on the GKS [A. Seidl, A. Görling, P. Vogl, J.A. Majewski, and M. Levy, Phys. Rev. B **53**, 3764 (1996)] or the GW [M.S. Hybertsen and S.G. Louie, *ibid.* **34**, 5390 (1986); X. Zhu and S.G. Louie, *ibid.* **43**, 14 142 (1991)].

- ²¹P. Dufek, P. Blaha, and K. Schwarz, Phys. Rev. B **50**, 7279 (1994).
- ²²J.K. Lang, Y. Baer, and P.A. Cox, J. Phys. F: Met. Phys. **11**, 121 (1981).
- ²³A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B 52, 5467 (1995).
- ²⁴A.B. Shick, A.I. Liechtenstein, and W.E. Pickett, Phys. Rev. B 60, 10763 (1999).
- ²⁵ W.E. Pickett, H. Krakauer, and P.B. Allen, Phys. Rev. B 38, 2721 (1988).
- ²⁶B.C. Chakoumakos, B.C. Sales, D. Mandrus, and G.S. Nolas, J. Alloys Compd. **296**, 80 (2000).
- ²⁷B.C. Chakoumakos, B.C. Sales, D. Mandrus, and G.S. Nolas, J. Alloys Compd. **322**, 127 (2001).
- ²⁸A. Bentien, B.B. Iversen, J.D. Bryan, G.D. Stucky, A.E.C. Palmqvist, A.J. Schultz, and R.W. Henning, J. Appl. Phys. **91**, 5694 (2002).
- ²⁹A. Bentien, A.E.C. Palmqvist, J.D. Bryan, S. Latturner, L. Furenlid, and B.B. Iversen, Angew. Chem., Int. Ed. Engl. **39**, 3613 (2000).
- ³⁰Y. Zhang, P.L. Lee, G.S. Nolas, and A.P. Wilkinson, Appl. Phys. Lett. **80**, 2931 (2002).
- ³¹N.P. Blake, D. Bryan, S. Latturner, L. Møllnitz, G.D. Stucky, and H. Metiu, J. Chem. Phys. **114**, 10 063 (2001).
- ³²K. Koepernik, B. Velický, R. Hayn, and H. Eschrig, Phys. Rev. B 55, 5717 (1997).
- ³³P. A. Cox, *The Electronic Structure and Chemistry of Solids* (Oxford University Press, Oxford, UK, 1991).
- ³⁴A. Bentien, V. Pacheco, S. Paschen, W. Carrillo-Cabrera, M. Baenitz, Y. Grin, and F. Steglich (unpublished).
- ³⁵S.E. Latturner, J.D. Bryan, N. Blake, H. Metiu, and G.D. Stucky, Inorg. Chem. **41**, 3956 (2002).
- ³⁶G. Cordier and P. Woll, J. Less-Common Met. 169, 291 (1991).