

## RAPID COMMUNICATION

## Why are Clathrates Good Candidates for Thermoelectric Materials?

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Received October 5, 1999; accepted October 11, 1999

**Clathrates are periodic solids in which tetrahedrally coordinated atoms form cages that surround a metal atom. We examine Slack's suggestion that the metal atoms scatter phonons but not electrons, thus lowering the thermal but not the electric conductivity. If this is true, as transport measurements indicate, these compounds are promising thermoelectric materials.** © 2000

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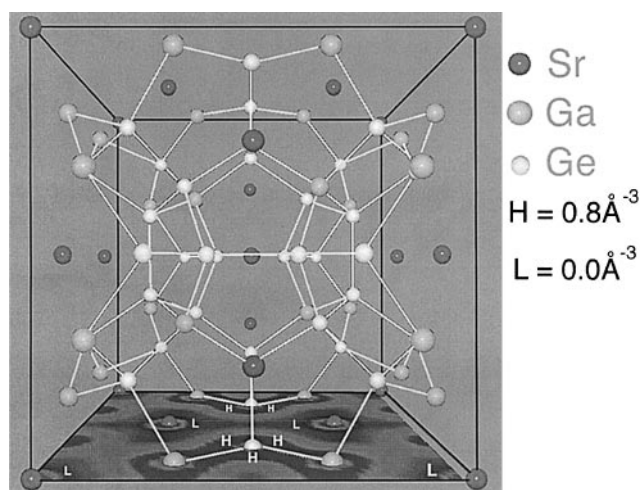
Thermoelectric materials are used for refrigeration and energy recovery, in special applications where small size, absence of moving parts, reliability, or environmental restrictions are important (1–4). The usefulness of a thermoelectric material increases as the dimensionless quantity  $ZT$ , where  $Z = S^2\sigma/\kappa$ , becomes larger (1–3). Here  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity,  $\kappa$  is the thermal conductivity, and  $T$  is the temperature. If we can find a material for which this ratio is equal to three or four, thermoelectric cooling can replace conventional methods of refrigeration (4).

Recently Slack (5, 6) has proposed a new criterion for finding better thermoelectrics. Based on examples, he argued that cage compounds with a large unit cell containing encapsulated atoms that can “rattle” inside the voids will have a low thermal conductivity. This advantage is offset if the modes effective in scattering phonons also scatter the conduction electrons, decreasing the electrical conductivity. What is needed is a material in which the encapsulated atoms scatter phonons but not conduction electrons. Slack called such a hypothetical material “a phonon-glass and an electron-crystal” (PGEC). A PGEC material is likely to have high electric conductivity and low thermal conductivity, if it has a decent Seebeck coefficient it will be a valuable thermoelectric.

One new class of candidates for PGEC materials are the compounds called *clathrates*. Their general formula is  $A_xB_yC_{46-y}$ , and their structure is shown in Fig. 1. The atoms  $B$  and  $C$  are tetrahedrally bonded to make a framework that forms cages around the guest atoms  $A$ . Examples are  $A_8C_{46}$  (with  $A = \text{Na, K, Rb}$  and  $C = \text{Si, Ge, Sn}$ ),  $A_8B_8C_{38}$  (with  $A = \text{Na, K, Rb}$ ;  $B = \text{Al, Ga, In}$ ;  $C = \text{Si, Ge, Sn}$ ), and  $A_8B_{16}C_{30}$  (with  $A = \text{Sr, Ba, Ca}$ ;  $B = \text{Al, Ga, In}$ ;  $C = \text{Si, Ge, Sn}$ ). If the metal atom rattles inside its cage, that will diminish the lattice thermal conductivity. If the electrical conductivity takes place mostly through the frame, then the rattling guest will not diminish the electrical conductivity.

Investigation of the transport properties of these compounds has begun only recently (7, 8). One of the more interesting among them is  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ . At room temperature, the best sample of Nolas *et al.* (7) has  $S = -320 \mu\text{V/K}$ , a resistivity of  $10.5 \text{ m}\Omega\text{-cm}$ , and  $\kappa = 0.9 \text{ W/mK}$ . The room-temperature  $ZT$  value is below that of the best commercial thermoelectric, but it is comparable to or better than that of other classes of compounds being studied in the hope of finding better thermoelectrics (4). Considering the large number of clathrates and the sensitivity of their transport coefficients to chemical modification, it is reasonable to hope that a good thermoelectric can be found among them.

The suggestion that the clathrates may provide examples of PGEC materials is most interesting, but other than transport data (7, 8) there is little direct evidence to support it. In fact, some of the current opinions concerning these compounds would suggest the opposite. It is commonly assumed that the metal atom in the cage donates electrons to the frame. If this is correct, the rattling ion will scatter the conduction electrons, lowering the conductivity; this effect would be particularly harmful if the electrical conductivity were to take place through the Sr atoms. If Sr is ionized, then  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  is not a PGEC material.



**FIG. 1.** The unit cell for the compound  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$ . The Ga site shown is one where 8 Ga are in the  $16I$  sites while the remaining 8 Ga are in  $24k$ . The contour map shows a  $[110]$  slice of the valence electron number density.

In this communication we use a maximum entropy method (MEM) (to analyze X-ray scattering data), together with density functional calculations (DFT), to show that  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  comes much closer to being a PGEC material than our present opinions about the chemical nature of the compound would suggest. We show that Sr atoms in the clathrate are practically neutral, that Sr is weakly bound to the cages and rattles around, that the electrical conductivity takes place through the frame, and that Sr-based bands do not contribute to the transport coefficients.

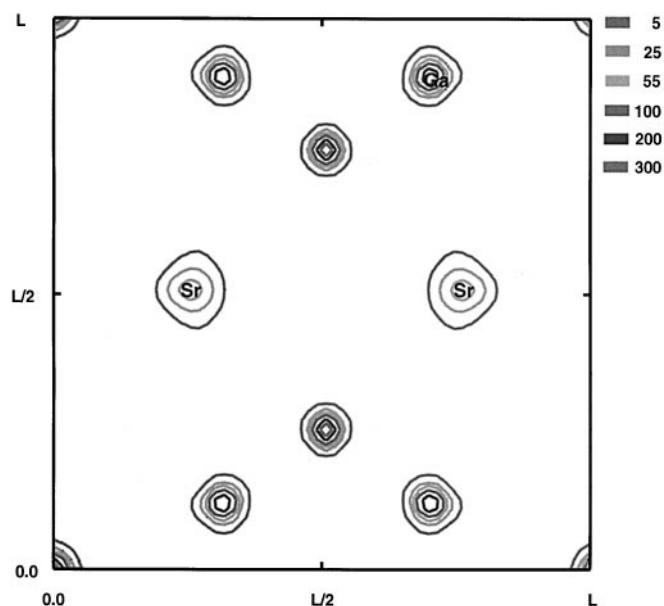
### THE STRUCTURE OF $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$

X-ray powder diffraction measurements were made on an  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  sample prepared as described by Nolas *et al.* (7). Full pattern Rietveld analysis was carried out with the refinement program GSAS (9). The unit-cell parameter of  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  thus determined is in good agreement with a previous study (10). Bond distance, bond angles, and other details will be given in a future article.

The structure factors extracted from the GSAS Rietveld refinement were used as input for maximum entropy method (MEM) calculations. Unlike the Rietveld analysis, MEM optimizes the intrinsic probability of a model structure without any prior assumptions, and it has been extensively tested in charge density reconstructions during this decade (11–14). We have calculated the MEM electron density distribution on a grid, with an iterative procedure, using the approximation introduced by Collins (15), as implemented in the MEED program (16). We found that use of structure-factor standard uncertainties calculated by the

GSAS program did not give convergence. We therefore introduced new standard uncertainties equal to the difference between observed and calculated structure factors after the Rietveld refinement. With these, convergence was quickly obtained. The resulting MEM densities have very low crystallographic reliability factors:  $R_F = 0.074$  at 20 K and  $R_F = 0.067$  at 298 K. The charge density produced by the MEM analysis is shown in Fig. 2. In this figure we have removed all the low-density contours that are not reliably determined from the present data; as a result we show the density of the core electrons and not that of the valence electrons. As we discuss below, this data and the DFT calculations indicate that Sr atoms undergo large-amplitude motion inside the cages, as postulated by Slack.

Density functional calculations with the generalized gradient approximation and ultrasoft pseudopotentials were performed with the Vienna Ab Initio Simulation Package (VASP) (17), using a plane wave cutoff of 174 eV. Since X-ray diffraction cannot easily distinguish Ga from Ge, a complete minimization was performed for several Ga geometries corresponding to different symmetry sites in  $Pm\bar{3}n$  (no. 223). The lowest energy structure has three Ga atoms occupying each of the 6-rings (50% occupancy of the  $6c$  sites, 18.75% occupancy of the  $16I$ , and 41.67% occupancy of the  $24k$  position). This structure agrees with the experimental observation that group III elements generally prefer to first enter the  $6c$  sites. The predicted cubic cell was 0.6% larger than experiment, while the calculated bond lengths deviated by an average of 0.5%.



**FIG. 2.** Experimentally determined core electron density (in units of  $\text{\AA}^{-3}$ ) for the  $[110]$  cut shown in Fig. 1. Note the anisotropic charge density around Sr(2).

## DO THE Sr ATOMS RATTLE?

The optimized structure has minimum energy when the Sr atoms are in the middle of the cages. To approximately determine the vibrational frequency of the Sr atoms, we calculated the change in the total energy when we displace Sr slightly and keep the cage rigid. The results are given in Table 1 for 0 and 300 K. The harmonic potential is anisotropic, and the amplitude parallel to the hexagonal windows is larger than the one perpendicular to it. The calculated frequencies are in agreement with estimates based on low-temperature thermal conductivity data (7, 8).

This large-amplitude motion ought to show up in the charge density determined by the MEM analysis of the X-ray data. And indeed it does. In Fig. 1 we show the calculated valence-electron density for a slice that passes through the middle of both the dodecahedral and the tetrakaidecahedral cages. Figure 2 shows the experimentally determined electron density at 298 K, in the cut through the crystal shown in Fig. 1. Here the anisotropy of the charge density of the Sr(2) is evident. In Fig. 1, there is no charge anisotropy around the Sr atoms. This suggests that the anisotropy in the measured charge density arises from vibrational motion. This assumption is consistent with the fact that the charge density from measurements performed at 20 K is less “smeared” than that obtained at 298 K. Estimates of the mean square displacement in the experimental data agree with the calculated ones.

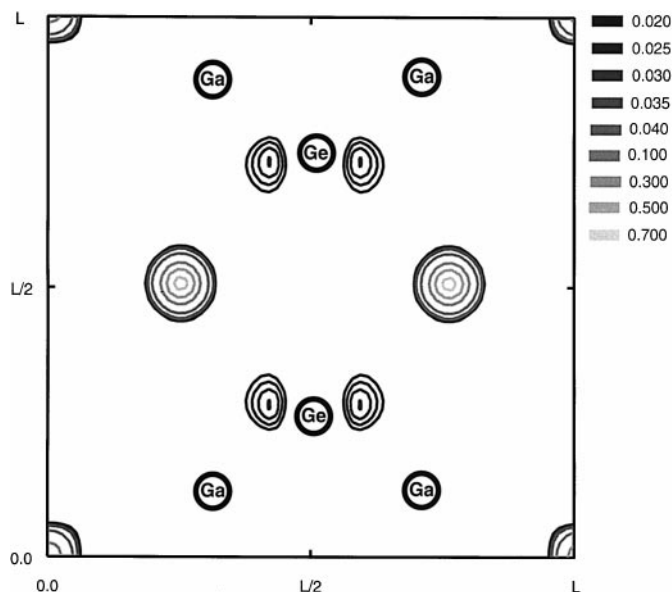
## ARE Sr ATOMS ELECTRON DONORS?

Here we examine whether or not the rattling of the Sr atoms is likely to be coupled to the conduction electrons. We expect this coupling to be strong if the Sr atom is ionized (as generally believed). Since the charge density derived from MEM is only accurate for densities in excess of  $1 \text{ \AA}^{-3}$ , experiment cannot help in determining valence charge densities ( $\rho < 0.8 \text{ \AA}^{-3}$ ). To determine the extent of charge donation we have therefore turned to theory. We have calculated several electron charge densities, the electron density  $\rho_c$  of

**TABLE 1**  
Calculated Frequencies and Root-Mean Squared Displacements for Sr in the 20-Atom Cages (Sr(1)) and 24-Atom Cages (Sr(2))

	$\omega$ ( $\text{cm}^{-1}$ )	$\langle r^2 \rangle^{1/2}$ (300 K) ( $\text{\AA}$ )	$\langle r^2 \rangle^{1/2}$ (0 K) ( $\text{\AA}$ )
Sr(2) <sup>⊥</sup>	62.29	0.144	0.056
Sr(2) <sup>  </sup>	20.02	0.447	0.098
Sr(1)	95.11	0.094	0.045

*Note.* The first and second rows correspond to Sr motion perpendicular to and parallel to the plane of the 6-ring. The root mean squared displacements are all calculated assuming a harmonic oscillator.



**FIG. 3.** The contours for positive Sr “charge transfer density”  $\rho_{CT}$  for the [110] cut shown in Fig. 1. The units are  $\text{\AA}^{-3}$ .

the clathrate, the electron density  $\rho_f$  of a hypothetical compound  $\text{Ga}_{16}\text{Ge}_{30}$  containing the frame atoms at the positions they have in the clathrate, and the charge density  $\rho_a$  of the hypothetical compound  $\text{Sr}_8$  consisting of *non-interacting* Sr atoms located at the positions they have in the clathrate.

To find whether there is charge transfer between the frame and the Sr atoms when the clathrate is formed, we examine the quantity  $\rho_{CT} = \rho_c - \rho_f - \rho_a$ . To understand this quantity, imagine a transformation in which the initial state consists of the hypothetical compounds  $\text{Sr}_8$  and  $\text{Ga}_{16}\text{Ge}_{30}$  and the final state is the clathrate. The quantity  $\rho_{CT}$  is the change in electron density when the system evolves from the initial to the final state. The regions where  $\rho_{CT}$  is negative are regions where electrons were removed from  $\text{Sr}_8$  and  $\text{Ga}_{16}\text{Ge}_{30}$  when the clathrate was formed. In the regions where electrons were added during the clathrate transformation,  $\rho_{CT}$  has positive values; the contour map for these values is shown in Fig. 3. In forming the clathrate, the electron density decreases between Sr atoms and increases in regions close to the Sr nuclei and to the Ge–Ga bonds. The electron density shift into the Ga–Ge bond occurs only for the bonds surrounding the large cages, where Sr(2) atoms are located.

To find out how much charge a Sr atom loses during this transformation, we have calculated the radial distribution of the electron density around the Sr nucleus. This shows that the *electron density* close to the Sr nuclei in the clathrate is *higher* than in the  $\text{Sr}_8$  compound. The integrated electron density distant from a Sr(2) atom in the clathrate is equal to 2 within a distance of  $3 \text{ \AA}$  from the Sr nucleus. This is similar to what we find for a free Sr atom and is a clear indication

that the Sr atoms in the clathrate are not ionized. Thus we do not expect the strong coupling between Sr and the frame electrons that would exist if the Sr were ionized. This is what Slack was hoping for, when he proposed that clathrates are PGEC materials.

### IS THE TRANSPORT TAKING PLACE THROUGH THE FRAME OR THROUGH THE Sr ATOMS?

Slack's proposal assumes that electrical conduction takes place through the frame. However, the Sr atoms in a clathrate form one-dimensional "wires" with an interatomic distance of 5.38 Å, and it is possible that these wires contribute substantially to the conductivity. If that is the case, then the large-amplitude motion of the Sr atoms will depress the conductivity and ruin the notion that the compound is an "electron crystal." The one-electron theory of transport allows us to determine if this is the case. Within this theory, the transport coefficients are expressed as a sum over the bands and the wave vector (18). It is therefore possible to calculate the contribution to the transport coefficients from each band. We did so and found that one band, just below the Fermi level, makes by far the largest contribution to both the Seebeck coefficient and the electric conductivity. Plots of the electron density of this band show that its electrons are located mainly around the Ge–Ga bonds. Thus, the main contribution to electric conductivity comes from the frame electrons; the orbitals containing contributions from the Sr atoms do not strongly affect the transport coefficients. The Sr bands are at and below the Fermi level, and their contribution to the Seebeck coefficient and electrical conductivity is very small, due to their low dispersion.

We also used the band structure to calculate the Seebeck coefficient and obtained  $-87.4 \mu\text{V/K}$  at 300 K. This is in reasonable agreement with the measured one, but care must be taken in comparing this to the experiment. The measured Seebeck coefficient depends rather strongly on the details of sample preparation and its theoretical value depends on the Ga siting. Nolas *et al.* (7) have shown that a small deviation from the ideal stoichiometry (i.e., by varying the Ga–Ge ratio) can change the Seebeck coefficient and resistivity by as much as a factor of four.

The computations show that  $\text{Sr}_8\text{Ga}_{16}\text{Ge}_{30}$  is a metal. In general, one expects metals to have a small Seebeck coefficient. This is not the case here because the compound has a sharp peak in the density of states at the Fermi level, which is known to lead to a large Seebeck coefficient. The high density of states also leads to an increase of the electronic contribution to the thermal conductivity. Fortunately, however, compounds can be synthesized such that the electronic

contribution to the thermal conductivity can be as low as only 6% of the total thermal conductivity, as estimated using the Wiedemann–Franz law (7).

Through a combination of experiments and theory, we have found that Sr atoms "rattle" in the structure and dissipate phonons, that the electrical conductivity takes place through the frame and not through the Sr "wires," and that Sr atoms are not ionized and do not couple to the conduction electrons. This means that  $\text{Sr}_8\text{G}_{16}\text{Ge}_{30}$  has the properties postulated for a PGEC material.

### ACKNOWLEDGMENTS

G.D.S., N.B., H.M., and A.E.C.P. greatly appreciate financial support of this work from the Office of Naval Research. B.B.I. gratefully acknowledges support from the Carlsberg Foundation and the Danish Research Councils. A.E.C.P. thanks STINT, the Swedish Foundation for International Cooperation in Research and Higher Education, for financial support. Use of beam line X7a at NSLS was supported by the U.S. Dept. of Energy, Division of Materials Sciences, under contract DE-AC02-98CH10886.

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