In this report we summarize the progress made since our last Scientific Report on clathrates [1] where we discussed the properties of Ba₆Ge₂₅ and Eu₆Ga₁₆Ge₃₀. Our main concern continues to be to discover new Kondo insulators in the family of clathrates or clathrate-like compounds. We have pursued this goal by different routes. An attempt was made to substitute Eu for Ba in Ba₆Ge₂₅ [2]. During this investigation a clathrate-like Eu phase, EuGa₂₆Ge₄₇ₓ was found and characterized in detail [3]. In order to suppress the ferromagnetism and to promote a strongly correlated semiconducting (Kondo insulating) ground state in Eu₈Ga₁₆Ge₃₀ we have, on one hand, varied the stoichiometry around the ideal 8:16:30 composition [4-6] and, on the other hand, we have performed high-pressure studies [7,8]. However, the ferromagnetic transition temperature turned out to be very robust against both influences. Several attempts to synthesize new rare-earth containing clathrates were unsuccessful. The synthesis of such compounds might be favored by high pressures. Therefore, considerable effort has been put into building up a high-pressure synthesis facility (see chapter “Synthesis at High Pressures and High Temperatures” in this Report). Even though we have, up to now, not found any Kondo insulating clathrate, our research has led to other very interesting findings.

In Ba₆-ₓEuₓGe₂₅, we have found a BCS-like superconducting transition at a resistive T_c ≈ 0.24 K, which increases more than 16-fold as the “locking-in” phase transition is suppressed by hydrostatic pressure [9]. A detailed investigation of the superconducting state of Ba₆Ge₂₅ and the isostructural compound Ba₅Na₂Ge₂₅ [9-11], band structure calculations [12], and optical reflectivity experiments [13] have shed new light on the influence of the locking-in phase transition on the electronic structure of Ba₆Ge₂₅.

The stoichiometry-tuning experiments on Eu₆Ga₁₆Ge₃₀ have shown that the (few) charge carriers present in all samples are due to off-stoichiometry and that Eu₆Ga₁₆Ge₃₀ samples with the ideal 8:16:30 composition would be insulators. Thus, we have shown the Zintl concept to be valid for Eu₆Ga₁₆Ge₃₀ [4,6]. Below we describe some of our results in more detail.

### Ba₆-xMₓGe₂₅ (M = Na, Eu)

Investigating the Ba-Eu-Ge system [2,3] we determined the solubility range of Eu in Ba₆Ge₂₅ [a ≈ 14.5565(2) Å]. For Ba₆-xEuₓGe₂₅ samples annealed at 630 °C the maximum substitution of Eu in the Ba sublattice is about 10% (x ≈ 0.6). In samples with x > 0.6, EuGe₂ and Ge appear as minority phases. The lattice parameter a varies linearly with the Eu content x at x < 0.6 but is constant at x > 0.6 (Fig. 1). Both Ba₆Ge₂₅ and Ba₅Eu₁₆Ge₂₅ melt incongruently (peritectically at about 816 °C and 806 °C, respectively). The sample Ba₅Na₂Ge₂₅ [a = 14.4703(2) Å] was also prepared but the homogeneity range of Ba₅-xNaₓGe₂₅ was not studied in detail [14]. Nevertheless, the study indicated that x = 2 represents the maximum Na solubility. An analysis of the crystal structure of Ba₅Eu₁₆Ge₂₅ [a = 14.5271(2) Å] shows that the Eu atoms preferentially occupy the Ba1 and Ba3
sites (21 % and 34 %, respectively) and that in Ba₄Na₂Ge₂₅ the Na atoms occupy only the Ba2 site. A splitting of the Ba2 and Ba3 sites as observed in Ba₆Ge₂₅ [1,2] is also found for Ba₄Eu₄Ge₂₅ and Ba₅Na₂Ge₂₅ [14]. In order to test whether this splitting occurs randomly or in an ordered way we have investigated Ba₆Ge₂₅ by high-resolution transmission electron microscopy (HRTEM). As may be seen from Fig. 2 no superstructure reflections and no inhomogeneity in the HRTEM image are observed, pointing to a random splitting at least at room temperature.

The two-step first-order locking-in phase transition, which occurs in Ba₆Ge₂₅ at $T_{S1,S2}$; 215, 180 K (average of warming and cooling curves), is quickly suppressed with increasing x in Ba₆₋ₓEuₓGe₂₅ and is absent altogether in Ba₅Na₂Ge₂₅ [2,9]. The rate of decrease of $T_{S1,S2}$ with decreasing lattice parameter $a$ is 5 times larger for Ba₆₋ₓEuₓGe₂₅ upon increasing x than for Ba₆Ge₂₅ under (small) hydrostatic pressure [2,9]. Also, Ba₅Na₂Ge₂₅ should, according to its lattice parameter, undergo a structural transition at $T_S$; 170 K. Thus, the suppression of $T_{S1,S2}$ by alloying Ba₆Ge₂₅ with Eu or Na is stronger than a mere chemical pressure effect. According to magnetization and magnetic susceptibility measurements Eu is close to the $f^1$ state in Ba₆₋ₓEuₓGe₂₅ [2]. It would be very interesting to obtain a full replacement of Ba at the Ba1 and Ba3 sites (or even at all three Ba sites) with Eu, i.e., Ba₆Eu₄Ge₂₅ (or Eu₆Ge₂₅) by the high-pressure synthesis to see whether Kondo lattice effects are observed. The fact that Ba locks into the split sites in Ba₆Ge₂₅ indicates that the guest/host interaction is stronger in Ba₆Ge₂₅ than in Eu₆Ga₁₆Ge₃₀, which does not behave as a Kondo lattice system.

Interplay of structural and superconducting transition in Ba₆Ge₂₅

The temperature dependence of the electrical resistivity $\rho(T)$ of Ba₆Ge₂₅ is presented in Fig. 3 for various pressures [9-11]. The main panel shows the high-temperature structural phase transition, the insets focus on the superconducting phase transition. The bulk nature of the superconductivity is inferred from measurements of the specific heat [9] and the magnetic susceptibility [11] in addition to this resistivity observation. At ambient pressure, $\rho(T)$ of Ba₆Ge₂₅ exhibits metallic behavior from room temperature down to about 230 K, followed at lower temperature by a two-step anomaly at $T_{S1,S2}$; 230 K, 196 K (on warming), which is due to the locking-in structural phase transition and which is accompanied by a steep increase of the resistivity to about 1 m$\Omega$cm. Below $T_{S2}$, the resis-

![Fig. 2: HRTEM image (Philips CM200 FEG) of Ba₆Ge₂₅ at room temperature, [111] zone, with simulated image (inset middle) and corresponding processed Fast Fourier Transform (FFT) (inset, left bottom). The change in contrast at the right top is due to crystal thickness and bending. The FFT pattern does not show any superstructure reflections.](image)

![Fig. 3: Temperature dependence of the electrical resistivity $\rho(T)$ of Ba₆Ge₂₅ at different hydrostatic pressures p.](image)
tivity continues to rise, saturating below 10 K at \( p_0 \); 1.5 m\( \Omega \) cm. At \( T_c \); 2 K, there is another strongly sample-dependent resistive anomaly which might originate from sample inhomogeneities and grain boundaries [11]. Finally, a BCS-like superconducting transition with the mid-point of the resistivity jump at \( T_c \); 0.24 K is observed [9,11]. With increasing pressure, the structural transitions are suppressed to lower temperatures and the residual resistivity \( \rho_0 \) is reduced. The low temperature anomaly disappears and \( T_c \) increases. At the critical pressure \( p_c = 2.8 \) GPa, where \( T_{S1,S2} \) are completely suppressed, \( T_c \) reaches a maximum of about 3.8 K above which the resistivity is metallic with a poor residual resistance ratio. With further increasing pressure \( T_c \) decreases slightly. Interestingly, we found [11] that \( T_c \) decreases exponentially as a function of \( \rho_0 \); \( T_c \propto \exp(-\rho_0/\rho_c) \), where \( \rho_c \) is a constant.

The pressure dependence of the structural transition temperatures \( T_{S1,S2} \) and the superconducting transition temperature \( T_c \) of \( Ba_6Ge_{25} \) are summarized in a lattice parameter (pressure) - temperature phase diagram (Fig. 4). The lattice parameters are calculated by using the bulk modulus \( B_0 = 44 \) GPa and its pressure derivative \( dB_0/dp = 5.8 \) [15]. \( T_{S1} \) (the onset temperature) and \( T_{S2} \) (the mid-point of the sharp resistive jump) are determined from the warming-up data. \( T_{S1} \) and \( T_{S2} \) decrease linearly with increasing pressure below 2 GPa and are rapidly suppressed by pressure above 2 GPa. On the other hand, \( T_c \) undergoes a 16-fold increase from \( T_c \) - 0.24 K at \( p = 0 \) to \( T_c \sim 3.85 \) K at \( p = p_c \sim 2.8 \) GPa as the structural transition is suppressed.

A comparison of the superconducting properties of \( Ba_6Ge_{25} \) with those of the iso-structural compound \( Ba_4Na_2Ge_{25} \) is most instructive. At ambient pressure, \( Ba_4Na_2Ge_{25} \) lacks the structural transition and becomes superconducting at a higher \( T_c \) of approximately 0.84 K. According to low-temperature specific heat measurements [9], the density of states \( N(E_F) \) inferred from the Sommerfeld coefficient is larger for \( Ba_4Na_2Ge_{25} \) than for \( Ba_6Ge_{25} \). Thus, the higher \( T_c \) of \( Ba_4Na_2Ge_{25} \) at ambient pressure can qualitatively be understood with the simple BCS formula \( T_c \ approximate \theta_D \exp(-1/N(E_F)V) \), \( \theta_D \) and \( V \) being the Debye temperature and the pairing potential, respectively. As the structural distortion of \( Ba_6Ge_{25} \) is suppressed by hydrostatic pressure, \( Ba_6Ge_{25} \) and \( Ba_4Na_2Ge_{25} \) behave similarly. However, \( Ba_6Ge_{25} \) now shows a much higher \( T_c \). These facts suggest that the structural transition may lead to a significant reduction of \( N(E_F) \) and therefore to a very low \( T_c \) at ambient pressure [9,11]. To test this idea, we have performed an upper critical magnetic field study of the electrical resistivities of \( Ba_6Ge_{25} \) and \( Ba_4Na_2Ge_{25} \) under hydrostatic pressure [11]. We found that the initial slopes of the upper critical field, \( \partial B_{c2}/\partial T \bigg|_{T_c} \), of both \( Ba_6Ge_{25} \) and \( Ba_4Na_2Ge_{25} \) are only weakly pressure dependent. In the ‘dirty’ limit, in which both samples were shown to be at all pressures [11], weak-coupling BCS theory gives \( \partial B_{c2}/\partial T \bigg|_{T_c} = (4490 \mathrm{Tm^2K^2/\Omega})\gamma T_c^{1/2} \). Since \( \gamma \propto \exp(\pi r_0^2/4\theta_D^2) \), we can determine the pressure dependence of \( N(E_F) \) from our experimental data of \( \partial B_{c2}/\partial T \bigg|_{T_c} \) and \( \rho_0(p) \). The result is shown in Fig. 5 [11]. Indeed, \( N(E_F) \) of \( Ba_6Ge_{25} \) increases by a factor of 4 as the structural transition is suppressed, whereas \( Ba_4Na_2Ge_{25} \) shows a weak increase of \( N(E_F) \) with increasing pressure. \( N(E_F) \) of the undistorted form of \( Ba_6Ge_{25} \) \( p \approx 2.8 \) GPa is larger than \( N(E_F) \) of \( Ba_4Na_2Ge_{25} \).

A detailed analysis [11] of the experimental data suggests that the pressure dependence of \( N(E_F) \) dominates the pressure dependences of \( T_c \) in \( Ba_6Ge_{25} \) for \( p < p_c \). As stated above, \( T_c \) can be nicely fitted by \( T_c \approx \exp(-\rho_0/\rho_c) \) as function of the residual resistivity \( \rho_0 \). Comparing this with the BCS for-

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**Fig. 4:** Lattice parameter (pressure) - temperature phase diagram of \( Ba_6Ge_{25} \). \( T_{S1,S2} \) designate the structural transitions; \( T_c \), the superconducting transition. For comparison, the superconducting transition temperature \( (20 \mathrm{~T}_c \) of \( Ba_4Na_2Ge_{25} \) is shown as a dotted line. The lattice parameter of \( Na_4Ba_2Ge_{25} \) at ambient pressure is denoted by a dashed line.
it follows that \( \rho_0 \approx 1/N(E_F)(p) \) if the Debye temperature \( \Theta_D \) and the pairing potential \( V \) are assumed to be pressure independent. In fact, the experimentally determined \( \rho_0(p) \) plotted vs. \( 1/N(E_F)(p) \) (from Fig. 5) does follow this \( \rho_0 \approx 1/N(E_F)(p) \) law. Also, \( T_c(p) \) plotted vs. \( 1/N(E_F)(p) \) may be well described by \( T_c = A \exp(-N/N(E_F)) \), where \( A \) and \( N \) are constants. Thus, the pressure dependence of \( N(E_F) \) alone can account for the strong enhancement of \( T_c \) as the structural distortion of \( \text{Ba}_6\text{Ge}_{25} \) is suppressed by pressure. Band structure calculations, to be presented below, show indeed the occurrence of a dip in the density of states at the Fermi level for distorted \( \text{Ba}_6\text{Ge}_{25} \), which is absent for the undistorted form of \( \text{Ba}_6\text{Ge}_{25} \).

**Band structure of \( \text{Ba}_6\text{Ge}_{25} \) and \( \text{Ba}_4\text{Na}_2\text{Ge}_{25} \)**

Our band structure calculations for the two clathrates, \( \text{Ba}_6\text{Ge}_{25} \) and \( \text{Ba}_4\text{Na}_2\text{Ge}_{25} \), were performed within the local density approximation (LDA) using the LMTO method within the atomic sphere approximation. A scalar relativistic version was used with a von Barth-Hedin exchange-correlation potential [12].

The overall band structure (Fig. 6) is similar to the one of Ge in the diamond-type structure. In the bonding region, the band structure resembles the one of hypothetical empty Ge cages. However, the conduction bands, in particular at the Fermi level, have a strong contribution of Ba states. The analysis of the \( l \)-projected DOS shows that these states are of strong \( d \)-symmetry character. The calculations yield a peak of the DOS at the Fermi level that hints at the structural instabilities of the system.

It is assumed that, at the phase transition, the Ba2 atoms in \( \text{Ba}_6\text{Ge}_{25} \) are (randomly) locked to split sites [2, 17]. We have examined this effect by shifting the Ba2 atoms to one of the split sites. This leads to a splitting of the above described peak and a reduction of the DOS at the Fermi level (Fig. 7). This splitting, being due to the shifting of Ba2 atoms and the corresponding symmetry lowering, may be considered as a band Jahn-Teller effect. It should be noted that we did not take into account the effect of the random disorder of the locked-in Ba atoms.

In \( \text{Ba}_4\text{Na}_2\text{Ge}_{25} \) there are also split sites, but there is no phase transition, i.e., no locking-in of either Ba or Na atoms, and it is plausible to perform the calculation keeping them at the average symmetric positions. Shifting Na or Ba atoms to one of the split positions does not produce a pronounced splitting of the peak in the DOS.

A locking-in of all Ba2 atoms in \( \text{Ba}_6\text{Ge}_{25} \) would result in a decrease of the value of the DOS by
about 25 (eV)\(^{-1}\) per unit cell, which corresponds to a drop of the Pauli susceptibility by 2.08 \times 10^{-4} \text{cm}^3/\text{mol} per formula unit, in order-of-magnitude agreement with the observed value. [2,17]. Moreover, the area of the Fermi surface is reduced because there are less bands crossing the Fermi level, as can be seen in Fig. 7. As a consequence, the electrical resistivity is expected to be enhanced below the locking-in phase transition, in agreement with the experimental observation.

The absolute value of the DOS at the Fermi level for distorted Ba\(_6\)Ge\(_{25}\) (with Ba\(_2\) shifted) is 25 (eV)\(^{-1}\) (half of the value for undistorted Ba\(_6\)Ge\(_{25}\)). This corresponds to \(\gamma = 15 \text{ mJ/molK}^2\) per formula unit. The experimental value is 21 mJ/molK\(^2\) per formula unit [9]. For Ba\(_4\)Na\(_2\)Ge\(_{25}\), we obtain 29 mJ/molK\(^2\) per formula unit, where the introducing value is 33 mJ/molK\(^2\) per formula unit. Introducing the calculated DOS values for distorted and undistorted Ba\(_6\)Ge\(_{25}\) in the BCS formula \(T_c \approx \Theta_d \exp(-1/N(E_f)V)\), a \(T_c\) ratio of 21 is obtained, in relatively good agreement with the observed ratio of 16. Thus, due to our band structure calculations, the DOS effect alone could account for the strong pressure variation of \(T_c\) in Ba\(_6\)Ge\(_{25}\).

Fig. 7: Electronic band structure and density of states around the Fermi energy once for Ba\(_2\) at the average position and once for Ba\(_2\) shifted 80% toward the split site in Ba\(_6\)Ge\(_{25}\). The dashed lines designate the bands that are crossing the Fermi level.

Fig. 8: Optical reflectivity \(R\) of Ba\(_6\)Ge\(_{25}\) at several temperatures: From bottom to top, \(T = 80, 140, 170, 200, 240, 295\) K. Inset: First derivative of the reflectivity \(dR/d\omega\). The dashed lines are Drude model fits as described in the text.

Optical reflectivity of Ba\(_6\)Ge\(_{25}\)

We have shown previously [2] that the Hall mobility \(\mu_h\) of Ba\(_6\)Ge\(_{25}\) decreases drastically as the system is cooled below the locking-in phase transition temperature. \(\mu_h\) is determined by the effective mass \(m^*\) and the relaxation time \(\tau\) via \(\mu_h \approx \tau m^*\). The reduction of \(\mu_h\) may be due to a decrease of \(\tau\) related to the enhanced disorder when Ba atoms lock randomly to split positions [9]. The results of our optical reflectivity measurements are shown in Fig. 8 [13]. A Drude-type electronic response, typical for systems with low charge-carrier concentration, dominates the reflectivity spectra at photon energies below 0.8 eV. We could fit the spectra with a Drude model with a temperature dependent plasma frequency \(\omega_p(T)\) but a temperature independent relaxation time \(\tau = (1.7 \pm 0.1) \times 10^{-13}\) s, as shown in the inset of Fig. 8. This would contradict our earlier assumption that the reduction of \(\mu_h\) is due to a decrease of \(\tau\) and would, instead, indicate that \(m^*\) increases. This interpretation is in agreement with the scenario of large bipolarons formed below the locking-in phase transition temperature proposed in Ref. 2. A low-temperature HRTEM investigation will be important to test whether the locking-in of the Ba atoms is really random.
Tuning the stoichiometry of Eu$_8$Ga$_{16}$Ge$_{30}$

The results described below will be published in a forthcoming paper [6]. Optical metallographic studies on a polished sample quenched from 1040 °C revealed that Eu$_8$Ga$_{16}$Ge$_{30}$ melts incongruently producing one majority and two minority phases.

The x-ray diffraction (XRD) pattern shows that the majority phase has the clathrate-I type structure [$a = 10.7059(1) \text{ Å}$]. The weak intensity of the reflections of the minority phases makes their identification very difficult. The energy dispersive x-ray (EDX) analysis gave a Ga-poor composition for Eu$_8$Ga$_{16}$Ge$_{30}$ (Fig. 10). The inset shows the variation of $n$ with the volume $V$ of the unit cell.

The XRD patterns show that Eu$_8$Ga$_{16}$Ge$_{30}$ crystallizes in one of the two possible structure types, clathrate-I or -VIII type, depending on the thermal treatment. Samples quenched from high temperature (1040 °C) and then annealed present the $\alpha$-Eu$_8$Ga$_{16}$Ge$_{30}$ structure (space group $I4\bar{3}m$, clathrate-VIII type structure) while slow cooling of melted samples up to the annealing temperature produces $\beta$-Eu$_8$Ga$_{16}$Ge$_{30}$ (space group $Pm\bar{3}m$, clathrate-I type structure). It was found that the lattice parameters $a$ of $\alpha$- (Fig. 9) and of $\beta$-Eu$_8$Ga$_{16}$Ge$_{30}$ (Fig. 10) correlate with the annealing temperature $T_a$. The variations are larger in the $\beta$ modification than in the $\alpha$ form: The maximal differences are 0.0043 Å and 0.0009 Å, respectively. Inspite of the rather large scattering of the $a(T_a)$ data for the $\alpha$ samples, one can identify a trend to have smaller $a$ at $T_a < 687 °C$ [$a = 10.6281(2) \text{ Å}$]. The smallest value of $a = 10.6272(1) \text{ Å}$ is found at $T_a = 650 °C$. $\alpha(T_a)$ of the $\beta$ samples shows a monotonous behavior. In contrast to the $\alpha$ samples, the smallest value of $a = 10.7056(2) \text{ Å}$ is observed at the highest $T_a = 697 °C$ for the $\beta$ samples. With decreasing $T_a$, $a$ increases and tends to a constant value of $a$; $10.7099(1) \text{ Å}$ at $T_a \approx 600 °C$. We assumed that different annealing temperatures cause different changes of the Ga/Ge ratio inside the narrow homogeneity range of Eu$_8$Ga$_{16}$Ge$_{30+x}$. The EDX analysis of 4 selected samples gives 8 Eu guest atoms and 46 Ga/Ge framework atoms per formula unit, as expected. However, a significant deviation from the starting Ga$_{16}$Ge$_{30}$ ratio is found, namely Eu$_8$Ga$_{15.5}$Ge$_{30.5}$ and Eu$_8$Ga$_{15.7}$Ge$_{30.3}$ for the $\alpha$ and $\beta$ phase, respectively. Thus, the $\beta$ phase is more Ga deficient than the $\alpha$ phase. The small differences in the Ga content among samples of the same structure type are difficult to detect. Nevertheless, the above discussed variation of $a$ indicates that a small homogeneity range between the Ga and Ge framework atoms does exist. An increase of $a$ with Ga content was observed for Sr$_5$Ga$_{16}$Ge$_{30+x}$ [18] and for Ba$_5$Ga$_{12}$Si$_{36}$ [$a = 10.4350(1) \text{ Å}$] and Ba$_5$Ga$_{12}$Si$_{33}$ [$a = 10.4705(2) \text{ Å}$] [19].

We have performed Hall effect measurements on both $\alpha$- and $\beta$-Eu$_8$Ga$_{16}$Ge$_{30}$. The charge carrier concentration $n$ was obtained from the Hall coefficient data at 2 K by correcting the data for the anomalous Hall effect and by using a one band model. It is surprising how well $n$ tracks the $a(T_a)$ dependence for the $\alpha$ samples (Fig. 9). For the $\beta$
Improved thermoelectric properties of stoichiometry-tuned $\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$

In order to investigate the influence of the off-stoichiometry on the thermoelectric properties of $\alpha$- and $\beta$-$\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$, we have measured the temperature dependences of the electrical resistivity $\rho(T)$, the thermopower $S(T)$, and the thermal conductivity $\kappa(T)$ of all samples exploited in Figs. 9 and 10. A detailed description of this work will be published in a forthcoming paper [5]. Our earlier results [1,20] were obtained on the $\alpha$ and the $\beta$ sample with the highest $T_a$ of 694 °C. $\rho(T)$, $S(T)$, and $\kappa(T)$ of the new samples annealed at $T_a < 690$ °C are in overall agreement with these earlier results. However, details of these properties vary systematically with the charge carrier concentration $n$, as we shall show below.

For all samples, $\rho$ increases with $T$ (positive $\rho/dT$), except for a narrow range above the ferromagnetic ordering temperature where ($\rho/dT$) is negative. For both the $\alpha$ and the $\beta$ sample series, this anomalous behavior becomes more pronounced with decreasing $n$. We have earlier associated the negative ($\rho/dT$) with the scattering of the charge carriers from critical magnetic fluctuations [20]. A better screening of these fluctuations in samples with higher $n$ is a plausible explanation for the above observation. The variation with $n$ of the residual resistance ratio $\text{RRR} = \rho(400 \text{ K})/\rho(2 \text{ K})$ and of the residual resistivity $\rho_0$ taken as $\rho$ at 2 K is shown in Fig. 11. There is a clear tendency that, for decreasing $n$, RRR decreases and $\rho_0$ increases, i.e., the samples become less metallic.

With increasing $T$, the absolute value of the thermopower $|S|$ increases for all samples. $S$ is negative in agreement with the charge carriers being electron-like. In Fig. 12 we show that the room temperature value of $|S|$ increases with decreasing $n$, as expected for a diffusion thermopower. At $n < 0.45$ electrons per unit cell, $|S|$ of $\beta$-$\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$ is almost twice as large as $|S|$ of $\alpha$-$\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$. This may indicate that the effective mass of the charge carriers is larger for $\beta$- than for $\alpha$-$\text{Eu}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$.

The temperature dependence of $\kappa$ is quite different for the $\alpha$ and the $\beta$ samples. For the $\alpha$ samples the electronic contribution $\kappa_e$, calculated from the electrical resistivity using the Wiedemann-Franz law, is less than 1 % of $\kappa$ at $T < 10$ K and about 30 % of $\kappa$ at room temperature. For the $\beta$ samples, $\kappa_e$...
is less than 15% of $\kappa$ below 10 K and about 50% of $\kappa$ at room temperature. The lattice contribution $\kappa_l$ of the $\alpha$-Eu$_8$Ga$_{16-x}$Ge$_{30+x}$ samples has a temperature dependence similar to the one observed for crystalline materials. However, below approximately 4 K, the expected $T^3$ dependence is not observed. Instead, $\kappa_l$ of the $\alpha$ samples shows a $T^e$ dependence with $e$ being 1.1 to 1.5, typical of structural glasses and clearly observed at low temperatures for Sr$_8$Ga$_{16}$Ge$_{30}$ [21] and Ba$_8$Ga$_{16}$Ge$_{30}$ [4]. $\kappa_l(T)$ of the $\beta$ samples is glass-like in the entire temperature range, in qualitative agreement with earlier published data [22].

The dimensionless thermoelectric figure of merit $ZT = S^2/\rho T \kappa$ calculated from the $\rho(T)$, $S(T)$, and $\kappa(T)$ data discussed above is shown in Fig. 13 for $T = 400$ K. For the $\beta$ samples, $ZT$ increases steeply with decreasing $n$, reaching $ZT \approx 0.4$ at $n = 3.5 \times 10^{26}$ m$^{-3}$. This is the highest $ZT$ value ever found for a clathrate. Further experiments will have to show whether the trend of increasing $ZT$ with decreasing $n$ continues for even lower $n$, which might result in $ZT \geq 1$ attractive for thermoelectric applications. For the $\alpha$ samples, on the other hand, $ZT$ is almost independent of $n$ and ranges between 0.29 and 0.35 for the samples investigated here. A discussion of possible reasons for the different thermoelectric properties of $\alpha$- and $\beta$-Eu$_8$Ga$_{16-x}$Ge$_{30+x}$ will be made in Ref. 5.

Can the ferromagnetic order be suppressed in Eu$_8$Ga$_{16}$Ge$_{30}$?

We have measured [5] the temperature dependence of the magnetic susceptibility $\chi(T)$ and the magnetic field dependence of the magnetization $M(H)$ of all samples of Figs. 9 and 10. $\chi(T)$ is Curie-Weiss-like above approximately 100 K, with effective moments which are in good agreement with the moment of free Eu$^{2+}$ for all samples. Also, the saturation magnetization $M_s$ at 2 K agrees approximately with the one expected for free Eu$^{2+}$ moments. Thus, we have no indication for a moment reduction due to the Kondo effect. The Curie temperature $T_C$ is almost the same for all the $\alpha$- (or $\beta$-) Eu$_8$Ga$_{16}$Ge$_{30}$ samples. This is rather surprising since we believe the ferromagnetism in Eu$_8$Ga$_{16}$Ge$_{30}$ to be due to the RKKY interaction, where a dependence of $T_C$ on the charge carrier concentration $n$ may be expected [20]. $T_C$ is also very robust against the application of hydrostatic pressure. It increases only slightly with pressure up to $p = 2.5$ GPa [7]. This is in accord with the smooth variation of the unit cell volume with pressure as determined from x-ray diffraction patterns of $\alpha$- and $\beta$-Eu$_8$Ga$_{16}$Ge$_{30}$ (Fig. 14) [8]. Thus, the ferromagnetism in Eu$_8$Ga$_{16}$Ge$_{30}$ cannot be appreciably influenced by the variations of $n$ and $p$ studied so far.
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