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Optical investigations of the clathrate α-$Eu_8Ga_{16}Ge_{30}$

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Abstract. We performed measurements of the optical reflectivity in the energy range 0.007–30 eV on the clathrate-VIII type compound α-$Eu_8Ga_{16-x}Ge_{30x}$ in order to investigate its electronic band structure. The very low charge carrier concentration as well as ferromagnetic ordering of the divalent Eu ions below 10.5 K characterize the spectra at photon energies below $\simeq$0.4 eV in accordance with the results of band structure calculations. Disorder induced bound states have been identified to affect the optical conductivity at energies between 10 and 100 meV.

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1 Introduction

Intermetallic clathrates, evolved from metal-stabilized silicon clusters [1], are open framework, novel, tunable electronic materials based on group-IV semiconductors and with the potential to form magnetic semiconductors. They are also believed to be basically new materials for effective thermoelectric devices as their properties combine glass-like heat conduction ('phonon glasses') with good electrical conduction ('electron crystals') [2].

The Eu-containing clathrate $Eu_8Ga_{16}Ge_{30}$ is made up of large cages of randomly distributed Ge and Ga atoms. The cages are fully occupied by Eu^{2+} 'guest' ions which order ferromagnetically at low temperatures and thus make this clathrate a local-moment ferromagnet. The structure of $Eu_8Ga_{16}Ge_{30}$ belongs in its α-modification to the cubic clathrate-VIII type with the space group $I\bar{4}3m$. Contrary to the β-modification the α-phase has only one type of cages centered by Eu atoms [3]. α-$Eu_8Ga_{16}Ge_{30}$ shows a Curie temperature as low as $T_C = 10.5$ K and an extraordinarily low charge carrier concentration [3]. Although not realized for the clathrates yet, the properties of the $Eu_8Ga_{16}Ge_{30}$ clathrates seem to indicate a route towards new kinds of so-called Kondo-Insulators [4,5].

From band-structure calculations α-$Eu_8Ga_{16}Ge_{30}$ and β-$Eu_8Ga_{16}Ge_{30}$ with an ideal Zintl stoichiometry are expected to be semiconductors [6]. However, the exact stoichiometry sensitively depends on the annealing conditions [7]. It was shown that the physical properties are closely related to changes in the (Ga,Ge)–composition [8,9]. α-$Eu_8Ga_{16}Ge_{30}$ could be prepared only with a slight deviation from the ideal Ga/Ge ratio α-$Eu_8Ga_{16-x}Ge_{30+x}$ [7,9]. As inferred from the normal Hall effect for $x > 0$, n-type electrical conductivity is established together with a low charge carrier density n. For $x = 0.48$ $n = 0.461$ e^-/(unit cell) (for unit cell volumes see Ref. [7]). A small anomalous contribution to the Hall effect, typical for ferromagnetic semiconductors, is found [3,7,9]. The electrical conductivity $\sigma(T)$ of α-$Eu_8Ga_{16-x}Ge_{30+x}$ shows metallic behavior (negative $d\sigma/dT$) in a large temperature range [3]. Above the ferromagnetic phase transition temperature a narrow anomaly with a positive $d\sigma/dT$ is found which may be due to scattering from critical spin fluctuations.

The knowledge of the electronic structure helps to understand the interplay of crystal structure, doping, magnetism and transport properties. Optical investigations of clathrates, focusing on the electronic band structure, have already been performed [10] and found to strongly support band structure calculations [11] for the chiral type clathrate Ba_6Ge_{25}. To our knowledge, analogous optical investigations of clathrate-VIII type structures are still lacking although their electronic band structure has been calculated [6]. This paper presents optical investigations on α-$Eu_8Ga_{16-x}Ge_{30+x}$ which provide not only results consistent with the calculated band structure but also insight into its metal-like behavior.

2 Experimental

In this paper we focus on the optical properties of α-$Eu_8Ga_{16-x}Ge_{30+x}$ whose preparation is described in

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detail in references [3,7]. We used a sample of the particular composition with $x = 0.42$. This value was determined by EDAX- and X-ray diffraction analysis together with Hall-effect results [3,7,9]. The off-stoichiometry makes the compound metal-like with a low charge carrier concentration of $n = 0.170\ e^-/(\text{unit cell})$. n was calculated from the Hall resistivity as a function of magnetic field at 2 K by assuming a one-band model [7,9].

We performed near-normal incidence reflectivity measurements on well polished, metallic-shining polycrystalline samples of α-$Eu_8Ga_{16-x}Ge_{30+x}$ with a 3 mm circular diameter surface. A rapid-scan Fourier spectrometer was used for energies $\hbar\omega$ between 7 meV ($60\,\text{cm}^{-1}$) and 1.5 eV ($12\,000\,\text{cm}^{-1}$). The sample was placed in a cryostat with a closed-cycle helium refrigerator operating in the temperature-range $7 < T < 300$ K. For determination of the reflectivity $R(\omega)$ we used as reference the sample itself after in-situ coating its surface with an evaporated gold film (thickness 1–3 μm). Synchrotron radiation (UVSOR, Institute for Molecular Science, Japan) was used to cover energies from 1.2 eV up to 30 eV [12]. The reflectivity was measured as a function of temperature below 3 eV and for higher energies at room temperature only.

Extrapolations of the form $R(\omega) \propto \omega^{-4}$ were used to complete the $R(\omega)$ spectra towards the high-energy end, and a Drude-Lorentz function towards the low-energy end. Using Kramers-Kronig relations, we were able to calculate the optical conductivity spectra $\sigma(\omega)$ from the optical reflectivity spectra [13]. Special care was taken on the low-energy extrapolation in order to fit the optical conductivity to the electrical conductivity in the zero energy limit, σ_{DC} (values from Ref. [9]). The Drude-Lorentz function was adjusted such that both σ_{DC} and $\sigma(\omega \leq 30\ \text{meV})$ were correctly described. A Hagen-Rubens approximation of the Drude-Lorentz function [13] failed to produce the correct values of σ_{DC}. This indicates for the Drude contribution small scattering times associated with disorder as discussed below.

3 Results and discussion

The measured reflectivity spectra $R(\omega, T)$ are shown for selected temperatures in Figure 1. A sharp drop of $R(\omega)$ around 0.1 eV separates a Drude-like charge carrier contribution at low energies from electronic interband transitions dominating the high-energy region. The Drude contribution terminates at a considerably low energy which is a direct consequence of the low charge-carrier concentration. Sharp features of phononic origin (with peak widths of the order of 1 meV) are hardly visible due to screening of the phonon excitations by conduction carriers.

Electronic excitations determine the reflectivity spectra and reflect the electronic band structure of α-$Eu_8Ga_{16-x}Ge_{30+x}$. The relation of the optical properties to band structure and σ_{DC} is best revealed by investigating the optical conductivity $\sigma(\omega)$. Figure 2 shows the real part $\sigma_1(\omega)$ of $\sigma(\omega)$ calculated from $R(\omega)$ as described above.

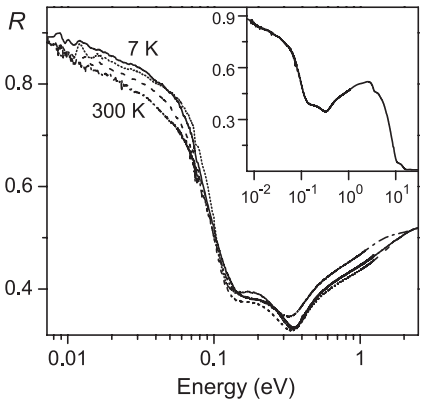

Fig. 1. Reflectivity spectra of α-$Eu_8Ga_{16-x}Ge_{30+x}$ ($x = 0.42$) at $T = 7, 20, 150, 300$ K. Inset shows the spectrum at $T =$ 300 K in the complete accessible spectral range.

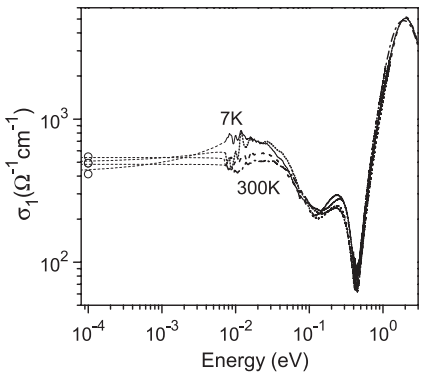

Fig. 2. Optical conductivity spectra of α-$Eu_8Ga_{16-x}Ge_{30+x}$ ($x = 0.42$) at $T = 7, 20, 150, 300$ K. At energies below 7 meV the dashed lines correspond to the low-energy extrapolation of the reflectivity spectra. The circles mark σ_{DC} measured at zero energy.

Three energy regions of $\sigma(\omega)$ may be discussed separately. The low-energy part starts with σ_{DC} (circles in Fig. 2) and continues with a Drude contribution which is dominating up to ≈0.01 eV. The region between 0.01 eV and 0.4 eV is characterized by two broad, temperature dependent, features indicating low-energy excitations in the system of charge carriers. The third region begins with the onset of interband transitions which are causing a strong increase of $\sigma(\omega)$ at ≈0.4 eV. This value is a measure of the gap between the valence and the conduction band in α-$Eu_8Ga_{16-x}Ge_{30+x}$ ($x = 0.42$) and is correctly reproduced by band-structure calculations [6].

As already indicated by the reflectivity spectra the optical excitation of conduction charge carriers is the main contribution to the low-energy part of $\sigma(\omega)$. The required consistency of $\sigma(\omega)$ with σ_{DC} (see circles in Fig. 2) causes a low energy peak feature at around 30 meV.

As mentioned above a low charge-carrier density n is characteristic for α-$Eu_8Ga_{16-x}Ge_{30+x}$ and leads to correspondingly low energies for the plasma edge. From $\sigma(\omega)$, a charge-carrier density n_{opt} may be derived. The effective charge-carrier concentration $N_{\mathit{eff}}(\omega_{\text{c}})$ which accounts for

optical excitations up to a cut-off frequency ω_c is obtained by the sum-rule argument

$$N_{eff}(\omega_c) = \frac{2m}{\pi e^2} \int_0^{\omega_c} \sigma_1(\omega')d\omega'. \quad (1)$$

We assume that n_{opt} is constituted by the charge carriers contributing to optical excitations up to $\hbar\omega_c = 0.13$ eV. Below this value $\sigma_1(\omega)$ strongly increases, rising to a maximum around 10 meV indicating a weakly bound electronic state as discussed below. Using both this assumption and equation (1) and further assuming a free-electron mass m_0 for the charge carriers we estimate $n_{opt} \simeq 0.22\ e^-$/(unit cell). This value corresponds to a Fermi energy $\epsilon_F = 118$ meV and agrees satisfactorily well with the result of Hall effect measurements $n_{Hall} = 0.170\ e^-$/(unit cell) [7,9], when taking into account a slightly enhanced effective mass m^* relative to m_0. Electronic band-structure calculations show that a small band mass is an inherent property of the type-VIII clathrate framework [6], in agreement with experimentally observed values [14].

Figure 3 provides a more detailed picture of what happens to $\sigma(\omega)$ when crossing the ferromagnetic ordering temperature $T_C = 10.5$ K. The main changes, emphasized by arrows, are almost insensitive to variations of the low-energy extrapolation of $R(\omega)$. The inset in Figure 3 displays the low-energy part together with a Drude-Lorentz data fit with Lorentz oscillators at 0.014 eV (width 0.057 eV) and 0.029 eV (width 0.064 eV) for $T = 7$ K and 20 K, respectively. Although the arrow-marked peak at 0.012 eV suggests a phonon excitation, in this energy region corresponding features could not be clearly resolved due to insufficient experimental accuracy. Low-energy vibrational modes have been reported in β-$Eu_8Ga_{16}Ge_{30}$ (type-I clathrate) at $\simeq$0.003 eV [15] and in $Cs_8Na_{16}Si_{136}$ (type-II clathrate) at $\simeq$0.007 eV [16]. They have been assigned to guest atom "rattling" which may cause resonant scattering of acoustic phonons.

The peak structures seen in Figure 3 below the band gap 0.4 eV at $\approx$0.03 eV and around 0.24 eV, respectively, strongly change shape and position when cooling through T_C. Within a 3% error margin, the spectral weight between 0.008 eV an 0.4 eV is preserved for the spectra at 7 K and 20 K. Hence, these peak structures are connected with intraband transitions which are significantly affected by the ferromagnetic ordering. Lowering T across T_C leads to a broadening of the peak structure at 0.24 eV and to a redistribution of spectral weight, see Figure 3. These values reflect transitions within the lower part of the conduction band as the Fermi-energy is rather small (according the low charge carrier density).

This change in the peak structures in the energy range 0.1 eV and 0.4 eV which is induced by the ferromagnetic ordering is consistent with the results of spin-dependent band structure calculations [6]. When crossing T_C, the T dependence of these peak structures reflects a shift of the spin-polarized band structure respective the Fermi level. These calculations revealed a large exchange splitting of

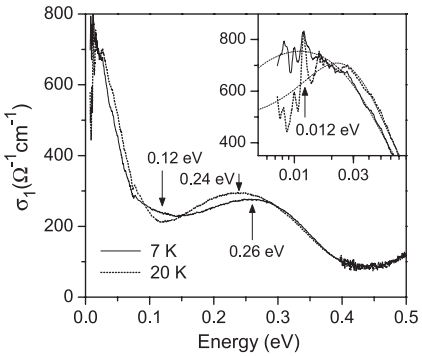

Fig. 3. Optical conductivity spectra of α-$Eu_8Ga_{16-x}Ge_{30+x}$ ($x = 0.42$) at $T = 7$ K and $T = 20$ K, below, and above T_C, respectively. Arrows and inset emphasize pronounced changes to $\sigma_1(\omega, T)$ when changing T across T_C. Inset: Enlarged view of the low energy part with a phononic feature at 0.012 eV. Thin dashed lines describe the spectra with a Drude-Lorentz oscillator.

the conduction bands ($\sim$0.36 eV) due to their hybridization with the unoccupied Eu $5d$ states. The Eu $4f$ states are too localized to overlap directly with the framework orbitals. They give rise to an only very small splitting ($\sim$0.05 eV) of the valence bands [6].

The low-energy peak structure as shown in the inset of Figure 3 appears at an energy that is very similar to the thermal activation energy of 15 meV of extrinsic donors in the structural homologous $Ba_8Ga_{16}Sn_{30}$ [14]. It may therefore be attributed to bound states within the band gap in α-$Eu_8Ga_{16-x}Ge_{30+x}$. Disorder associated with the random positioning of the Ga- / Ge-atoms could generate these bound states providing a large scattering cross-section for charge carriers. This is nicely confirmed by the observed relative smallness of the Hall mobility in α-$Eu_8Ga_{16}Ge_{30}$ [3,7,9] where, as mentioned above, m^* is only slightly enhanced compared to m_0. Also, as mentioned above, the failed Hagen-Rubens approximation of the low energy reflectivity data indicates small scattering times or large scattering rates.

4 Conclusion

In summary, we have measured the near normal incidence reflection on α-$Eu_8Ga_{16-x}Ge_{30+x}$ of the particular composition with $x = 0.42$ in a wide spectral region at temperatures above and below the ferromagnetic phase transition temperature, $T_C = 10.5$ K. The low-energy Drude type of optical conductivity is characterized by a very low charge carrier density $n_{opt} \simeq 0.22\ e^-$/(unit cell), in accordance with the results of Hall-effect measurements [3]. The low-energy region 0.1–0.4 eV is characterized by transitions within the lower end of the conduction band, in agreement with band structure calculations which also correctly predict the valence-conduction band gap as observed (>0.4 eV) [6]. At energies between 10 and 100 meV, pronounced broad peak structures are assigned to excitations from disorder-derived bound states within the band

gap reflecting the random distribution of the Ga- and Ge-atoms in the clathrate network [8,9]. By lowering the temperature across T_C, the shifting of the Fermi level in the exchange-split conduction band causes the peak structures in the optical conductivity to change in shape and position at energies below 0.4 eV, whereas the spectral weight is conserved in this energy region.

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