OPTICAL REFLECTIVITY OF THE CLATHRATE COMPOUND Ba_6Ge_{25}*

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We report optical investigations of the electronic properties of the clathrate compound Ba_6Ge_{25} in which at room temperature Ba atoms "rattle" in Ge-network cavities. When lowering the temperature across $T_S \simeq 200\,K$ a lock-in of the Ba-atoms to split-site positions in the cages is observed. The low energy Drude type of reflectivity is characterized by a low charge carrier density which smoothly varies with temperature. However, the Drude relaxation time of the charge carriers is found to be almost temperature independent, especially when cooling below T_S where, according to thermopower data, the effective mass is enhanced. This behavior could indicate a formation of polaronic quasi particles below T_S which is also supported by previous measurements of magnetic susceptibility of Ba_6Ge_{25}.

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1. Introduction

On the search for small-gap semiconductors/semimetals Kondo Insulators (KI) [1] the new clathrate compound Ba_6Ge_{25} was recently discovered [2] and may be considered as a reference compound for a potential KI when the Ba atoms are substituted by suitable rare earth elements with an unstable $4f$ shell [3]. Ba_6Ge_{25} is a system with a relatively low charge carrier density which, near $T_S \simeq 200\,K$, undergoes a metal to semiconductor-like transition as well as a change of Ba-displacements and becomes superconducting at

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$T_c \simeq 0.24\,\mathrm{K}$ [4,5]. The cubic structure consists of large cages of germanium which encapsulate the Ba atoms. Some of the Ba atoms are locked into split positions below T_S. This behavior crucially effects the superconducting phase transition and the properties of the charge carriers which propagate within the framework of cages. We performed near-normal incidence reflectivity measurements on well polished polycrystalline samples of Ba_6Ge_{25}. A Bruker rapid-scan Fourier spectrometer was used for energies between 5 meV ($40\,\mathrm{cm}^{-1}$) and 3 eV ($22000\,\mathrm{cm}^{-1}$). Synchrotron radiation was used to cover energies from 1.2 eV up to 30 eV. The sample was placed in the exchange gas of a ^{4}He bath cryostat allowing for temperatures $2 < T < 300\,\mathrm{K}$.

2. Results and discussion

Fig. 1 shows the temperature dependence of the electrical resistivity ρ which near T_S strongly changes between metallic (above T_S) and semiconductor-like (below T_S) behavior. A distinct thermal hysteresis of the resistivity evidences a first order phase transition. From Hall-effect measurements the charge-carrier concentration $n(T)$ has been determined within a one-band model. The inset of Fig. 1 shows $n(T)$ with a remarkably weak temperature dependence at T_S. Therefore the charge carrier mobility μ is supposed to be responsible for the strong change of the electrical conductivity at T_S. Indeed, at T_S, the Hall mobility $\mu_H(T) = R_H/\rho$ changes in the same way as $1/\rho(T)$ does [4].

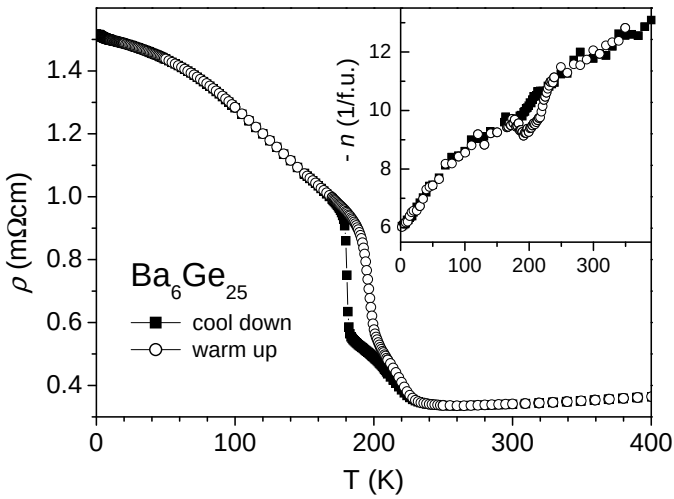

Fig. 1. Electrical resistivity $\rho(T)$ of Ba_6Ge_{25}. Inset: Temperature dependence of the (negative) charge-carrier concentration $-n(T)$ as determined by Hall measurements (f.u. $\equiv$ formula unit Ba_6Ge_{25}).

The charge carrier mobility μ_H is determined by the effective mass $m^\star$ and the relaxation time τ via $\mu_H \propto \tau/m^\star$. When lowering the temperature one may expect τ to decrease significantly when crossing the phase transition temperature $T_S \approx 200\,K$. This is because no inter cell correlations of the Ba atomic displacements were found and therefore the resulting disorder should lead to strong random scattering [5]. On the other hand $m^\star$ could also be increased below T_S due to changes in band structure. To disentangle the effects of $m^\star$ and τ on the mobility, investigations of the optical reflectivity can help as the time scales of relaxation time ($\sim 10^{-14}$ s) and optical frequencies coincide.

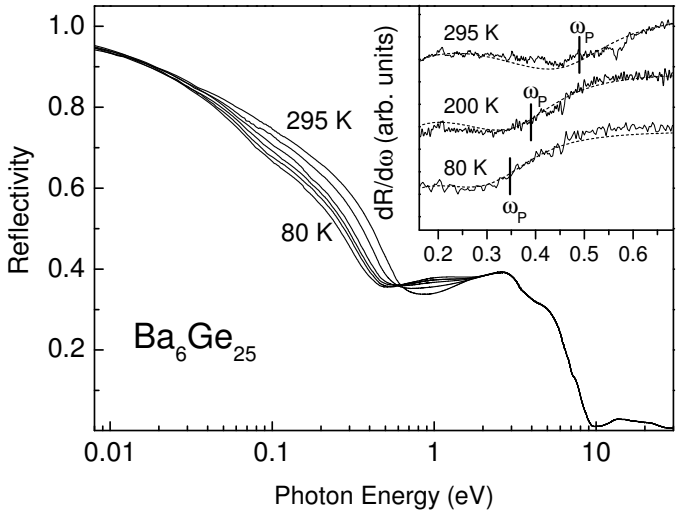

Fig. 2. Optical reflectivity R of Ba_6Ge_{25} at several temperatures: from bottom to top, T = 80, 140, 170, 200, 240, 295 K. Inset: First derivative of the reflectivity $dR/d\omega$. The dashed lines are Drude model fits with the following parameters: a plasma frequency ω_P (values indicated in the figure) and a temperature independent relaxation time $\tau = (1.7 \pm 0.1) \times 10^{-14}$ s.

An electronic response which is typical for systems with low charge carrier densities dominates the reflectivity spectra shown in Fig. 2. The low-energy Drude-like part of the reflectivity is characterized by temperature dependent plasma frequencies with values smaller than $\omega_P \approx 0.5$ eV which corresponds to about 5 electrons per Ba_6Ge_{25} unit (assuming a free electron mass). For $\omega < 0.6$ eV the temperature dependent reflectivity spectra look very similar in shape and only their edges at around 0.5 eV vary smoothly with temperature. This is in accordance with the smooth and almost linear behavior of $n(T)$ (inset of Fig. 1) if these edges are interpreted as plasma edges in a Drude response, $\omega_P^2 \propto n/m^\star$. Moreover, no differences of the

reflectivity spectra between cool down and warm up at $T \approx T_S$ are observed which agrees well with the weak hysteresis of $n(T)$ around T_S. The influence of $m^\star$ on ω_P will be analyzed in future within a Drude–Lorentz model taking into account band-structure calculations.

The slope of the plasma edges is characterized by the Drude relaxation time. As can be seen in the inset of Fig. 2 the slopes could be described by a temperature independent Drude relaxation time $\tau = (1.7 \pm 0.1) \times 10^{-14}$ s. Especially when crossing the phase transition temperature T_S the relaxation time seems to be not much affected. This is in contrast to assumptions to understand the anomalously low bare density of states in the distorted low-temperature phase of Ba_6Ge_{25} [5].

To understand this observation one could think of a different kind of quasi particles below T_S. From susceptibility measurements [5] there is evidence for the formation of spinless bipolarons: below T_S the magnetic susceptibility is reduced by the free electron Pauli contribution. Large bipolarons give rise to band-like transport [6] as observed in measurements of the electrical resistivity and Hall-effect [4]. Moreover, thermopower data support this picture as they may be interpreted as evidence for an increase of the effective charge carrier mass below T_S [4].

A reduction of a purely electronic type of conduction is also indicated in our optical data by a spectral weight transfer from low energies to a peak at around 1 eV (see Fig. 2) concomitant with the enhancement of the effective carrier mass.

In conclusion from measurements of the optical reflectivity we found an almost temperature independent charge carrier relaxation time when crossing the temperature $T_S \approx 200$ K, where Ba atoms lock-in to presumably randomly distributed split positions in Ge-network cavities. Together with results of magnetic susceptibility and thermopower measurements our optical data at energies below 2 eV seems to provide evidence for excitations of large bipolarons. Further optical investigations and data analysis in this direction are currently in progress.

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