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Glasslike excitations in single crystalline $Sr_8Ga_{16}Ge_{30}$ clathrates

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Abstract

Low-temperature ultrasonic attenuation and resonant ultrasound spectroscopy (RUS) data are reported on single crystals of the semiconductor $Sr_8Ga_{16}Ge_{30}$. The attenuation shows a strikingly glasslike behavior, implying that the elastic properties of the clathrate crystal at low temperatures ($T<1$ K) are dominated by the presence of tunneling states. At slightly higher temperatures, the RUS data reflect the presence of a 2-level system with an energy-spacing of 45 K. The origin of these low-energy excitations is found in the 'rattling' Sr-atom, which occupies a fourfold split site in the clathrate structure. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Elastic properties; Tunneling states; Clathrates

1. Introduction

The low-temperature thermal and elastic properties of glasses are known to be quite different from those of perfect crystals [1]. They are successfully described by the Tunneling Model, which postulates the existence of low-energy excitations (the so-called tunneling states), with an energy-independent density of states $\bar{P}$ [2]. Some disordered crystals and quasicrystals have properties very similar to those of glasses (for recent reviews, see Ref. [3]). Mixed alkali-halide cyanides $(MX)_{1-x}(M(CN))_x$, where M refers to an alkali metal and X refers to a halide atom, are probably the best known examples of disordered crystals with glasslike low-temperature properties [4]. Disorder produced by simple monatomic substitution does not lead to glasslike lattice vibrations, but if the substitutional atoms have a different charge, a large concentration of vacancies or interstitials will be created and this type of disorder *can* produce glasslike behavior, as is observed in the fluorite structure crystals $Zr_{1-x}Y_xO_{2-x/2}$ [5]. Recently, several compounds have been identified that combine the high electron mobilities of crystals with the low thermal conductivities characteristic of glasses [6]. The common structural feature of these "phonon-glass electron-crystals" (PGECs) is that they contain loosely bound atoms that reside in a large crystalline "cage". A particular class of PGECs is formed by the filled skutterudite antimonides, derived from a regular unfilled skutterudite such as $CoSb_3$,

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by "filling" the void in the skutterudite structure by a lanthanide [7]. The presence of the rare-earth leads to glasslike thermal properties, complemented by an unusual thermodynamic behavior that indicates the presence of at least two low-energy vibrational modes in addition to the normal acoustic phonons [8]. $Sr_8Ga_{16}Ge_{30}$, a Ge-clathrate, is another example of a PGEC, combining a low thermal conductivity, characteristic of a glass, with relatively high electron mobility [9]. In this paper, we report ultrasonic attenuation measurements at low temperatures (0.3–10 K) and resonant ultrasound spectroscopy (RUS) data as a function of temperature (2–300 K) on single crystalline $Sr_8Ga_{16}Ge_{30}$. The results reveal a new category of single crystals with low-temperature properties that were believed to exist only in amorphous and disordered solids.

2. Experimental details

$Sr_8Ga_{16}Ge_{30}$ single crystals were synthesized at Oak Ridge National Laboratory, by melting stoichiometric quantities of high-purity elements in carbon-coated sealed and evacuated silica tubes [10]. A high-quality crystal was cut into a rectangular bar of approximately $8 \times 2 \times 1\,mm^3$. Because the sample was too small to be cut into an oriented bar, none of the sides of the bar correspond to a principal crystallographic direction. On this sample, measurements of the ultrasonic attenuation were performed as a function of temperature (0.3–10 K) at 2 frequencies: 155 and 250 MHz. These measurements were carried out using a pulse-echo technique. A second sample was prepared for RUS measurements. RUS is a novel technique for determining the elastic moduli of solids, based on the measurement of the resonances of a freely vibrating body [11]. The mechanical resonances can be calculated for a sample with known dimensions, density, and elastic tensor. In an RUS experiment, the mechanical resonances of a freely vibrating solid of known shape are measured, and an iteration procedure is used to 'match' the measured lines with the calculated spectrum. This allows determination of all elastic constants of the solid from a single frequency scan, which clearly indicates a main advantage of RUS: there is no need for separate measurements to probe different constants, and multiple sample remounts and temperature sweeps are avoided. The sample is lightly held at opposite corners between two transducers, eliminating bonding agents that can be particularly bothersome at low temperatures. Another advantage lies in the ability of RUS to work with small samples: whereas conventional techniques can demand a sample-size up to a centimeter, RUS measurements can be made on mm-sized samples. The RUS data reported here were carried out as a function of temperature (2–300 K) on an oriented parallelepiped of approximately $1.5 \times 2 \times 2.5\,mm^3$.

3. Results and discussion

Fig. 1 shows the shear modulus c_{44} for $Sr_8Ga_{16}Ge_{30}$, obtained from RUS measurements. 'Normal' elastic behavior can be modeled with the so-called Varshni function [12], and shows a monotonic increase with temperature, leveling off at low temperatures. The elastic response of $Sr_8Ga_{16}Ge_{30}$ is rather unusual, showing a modest 'dip' around 30 K. The upper panel of Fig. 1 illustrates that this 'dip' cannot be modeled with the Varshni function. A similar behavior was observed in filled skutterudites, which could be modeled assuming the presence of two isolated 2-level systems [8]. Attempting to model the $Sr_8Ga_{16}Ge_{30}$ data, we used the approach that was successful for the skutterudites, calculating the elastic response of a 2-level system and adding that to a background Varshni. Assuming that the level spacing Δ depends linearly on the strain, the elastic data can be modeled quite well by using one 2-level system with a spacing of 45 K, as shown in the lower panel of Fig. 1. This is in excellent agreement with specific heat measurements [10]. Sales et al. [10] showed that below 80 K, the specific heat in $Sr_8Ga_{16}Ge_{30}$ deviates from normal Debye behavior. A low-energy Einstein mode with characteristic energy of 53 K has to be added to describe the influence of the 'rattling' Sr-atom. A systematic study of the elastic constants of other

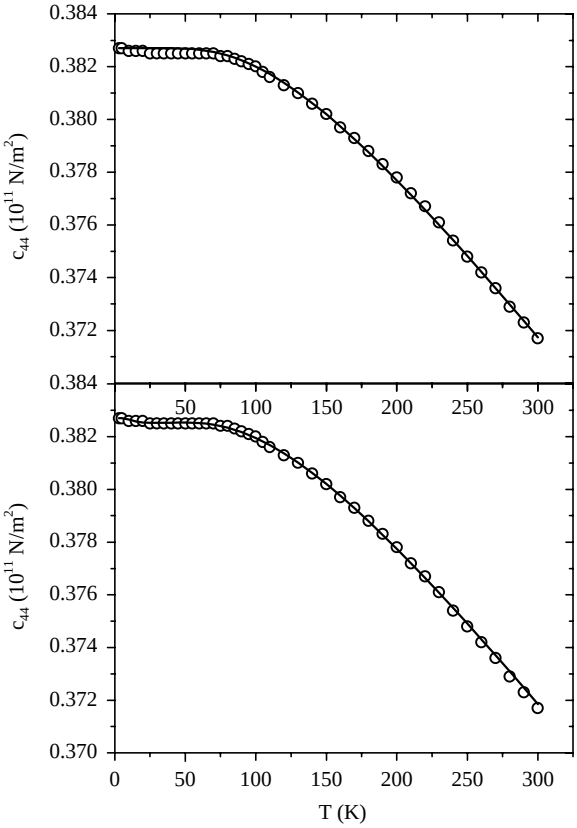

Fig. 1. Shear modulus c_{44} for $Sr_8Ga_{16}Ge_{30}$. The solid line is a model calculation using the Varshni function only (upper panel) and using the Varshni function together with a 2-level system with a characteristic energy of 45 K (lower panel).

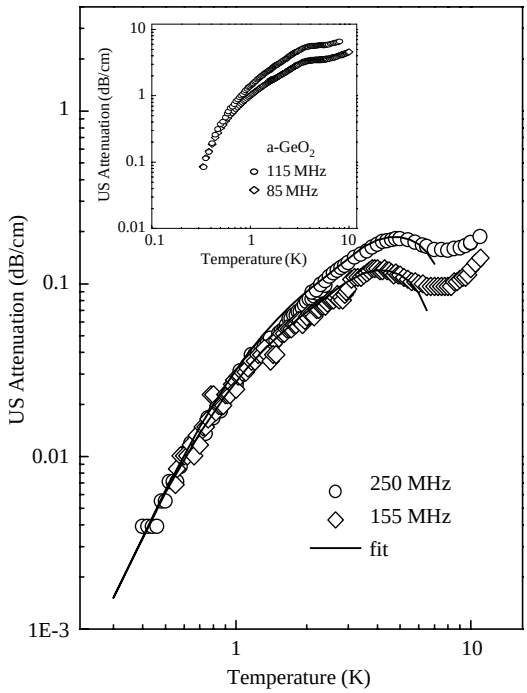

Fig. 2. Ultrasonic attenuation as a function of temperature for $Sr_8Ga_{16}Ge_{30}$. The inset shows the attenuation for a-GeO_2.

Ge-clathrates is currently being carried out, and the results will be published elsewhere.

Fig. 2 shows the ultrasonic absorption for $Sr_8Ga_{16}Ge_{30}$, after subtracting a temperature-independent residual attenuation, α_0, due to geometrical factors. The temperature-dependence of the attenuation at the lowest temperatures clearly shows a non-crystalline behavior: in a single crystal, changes in the US attenuation are expected to be negligibly small below a few degrees Kelvin. Instead, the attenuation in the clathrate crystal below 1 K clearly rises with increasing temperature, showing a T^3 dependence. This is remarkably similar to what is generally found in amorphous materials. The inset of Fig. 2 shows the US attenuation for a representative glass, a-GeO_2: a T^3 dependence is observed at the lowest temperatures, leveling-off to a temperature independent plateau above a few K. While the T^3 at the lowest temperatures is frequency independent, the height of the plateau increases linearly with frequency. This behavior is typical for amorphous materials, where it is attributed to the interaction of the phonons with tunneling states [1]. It is remarkable how the attenuation in the single-crystal clathrate follows the predictions of the tunneling model at the lowest temperatures. This suggests that the US absorption in the crystalline Ge-clathrate is dominated by glasslike tunneling states and agrees with thermal conductivity (κ) data [13]: thermal conductivity measurements on polycrystalline $Sr_8Ga_{16}Ge_{30}$ showed a glasslike temperature dependence, and indicated the possible presence of tunneling states. The attenuation measurements on single crystalline $Sr_8Ga_{16}Ge_{30}$ confirm the observations of Cohn et al. [11], and rule out that the grain boundaries are the source for the glasslike κ in the polycrystal. At higher

temperatures (>1 K), the attenuation departs somewhat from what is expected based on the tunneling model: according to the model, the T^3 dependence of the attenuation levels-off to a temperature-independent 'plateau', the height of which increases linearly with frequency. Such a plateau is indeed observed in most amorphous solids. The clathrate crystal, however, shows a pronounced maximum where the plateau is expected. To the best of our knowledge, such a distinct maximum has been reported only once [14]: US attenuation measurements in neutron-irradiated quartz that had been subject to heat treatment showed a pronounced maximum, where prior to heat-treatment a plateau was observed. In what follows, we will try to investigate the possible significance of the maximum. Therefore, the basic idea and assumptions behind the tunneling model will be examined. As mentioned above, this model assumes the existence of low-energy excitations, the so-called tunneling states (TS), with a wide distribution of energies and relaxation times. These TS arise from atoms or groups of atoms with two possible equilibrium positions with nearly equal energy. They are formally presented as particles moving in an asymmetric double well. The energy difference between the eigenstates is given by $E=(\Delta^2+\Delta_0^2)^{1/2}$, with Δ the asymmetry of the double well; Δ_0 is the tunnel splitting and can be written as $\Delta_0=\hbar\Omega\exp(-\lambda)$ where λ describes the overlap of the wave functions. One of the basic assumptions of the tunneling model is that Δ and λ are independent of each other and have a broad and uniform distribution $P(\Delta,\lambda)=\bar{P}\mathrm{d}\Delta\mathrm{d}\lambda$, with $\bar{P}$ a constant, the density of states of the TS. Since $\lambda=(d/\hbar)\sqrt{(2\,\mathrm{mV})}$ depends on quantities such as the mass m of the tunneling particle, the height V of the potential barrier, and the distance d between the minima of the double well, a uniform distribution of λ seems to be rather unlikely. Nevertheless, it is in good agreement with experimental results in amorphous materials. According to the tunneling model, an elastic wave changes the splitting of the asymmetric double-well potentials of the TS. In absence of free electrons, the return to equilibrium will occur via interaction with thermal phonons. At low temperatures, the most likely process is the one-phonon process, with a relaxation rate τ^{-1} [1]:

$$\tau^{-1}=K_3(\Delta_0/E)^2(E/2k)^3\coth(E/2kT) \tag{1}$$

with $K_3=(4k^3/\rho\pi\hbar^4)\sum_i\gamma_i^2/v_i^5$, ρ is the mass density, v is the speed of sound. K_3 describes the coupling of the TS with the phonons, taking into account all polarizations and directions. The general expression for α due to this process can be calculated numerically and can be written as

$$\alpha=\frac{\gamma_l^2}{\rho v_l^3kT}\int_{E_{\min}}^{E_{\max}}\mathrm{d}E\int_{u_{\min}}^{1}\frac{\omega^2\tau}{1+\omega\tau}\frac{\bar{P}}{u(1-u^2)^{1/2}}\left(\frac{\Delta}{E}\right)^2\times\operatorname{sech}^2\left(\frac{E}{2kT}\right)\mathrm{d}u \tag{2}$$

with $u=\Delta_0/E$. Analytic solutions can be derived for the limiting cases $\omega\tau_m\gg1$ and $\omega\tau_m\ll1$ (with τ_m the smallest relaxation time of the TS). At low temperatures, the relaxation rate of the TS is small compared with the angular frequency of the applied strain ($\omega\tau_m\gg1$), and the occupation of the TS are incapable of reaching equilibrium on the time scale of the oscillation. This leads to a T^3 dependence of the attenuation:

$$\alpha=\frac{\pi^4}{96}\frac{\bar{P}\gamma_l^2}{\rho v_l^3}K_3T^3.$$

At higher temperatures, where the TS relax quickly enough to reach equilibrium on the time scale of the oscillations ($\omega\tau_m\ll1$), the attenuation is temperature-independent (the 'plateau') and increases linearly with frequency:

$$\alpha=\frac{\pi}{2}\frac{\bar{P}\gamma_l^2}{\rho v_l^3}\omega.$$

The temperature-independent plateau is a direct consequence of the broad (Δ,λ)-distribution: since the relaxation rate τ^{-1} of the TS is proportional to $(\Delta_0/E)^2$ (Eq. (1)), a given value of E implies a distribution of τ^{-1}. If all TS would relax with the same relaxation time, the attenuation would be sharply peaked by the factor $\omega^2\tau/(1+\omega^2\tau^2)$, but due to the broad distribution of relaxation times, all relaxation times that fulfill the condition $\omega\tau=1$ will contribute, leading to the plateau. This means that the observed maximum could be caused by a significant reduction of the τ distribution. For heat-treated neutron-irradiated quartz, the maximum could be successfully

analyzed with a slightly modified tunneling model, using a uniform but restricted λ distribution [12]. Such a cut off may be rather crude, but it models the data after heat treatment quite well, the derived parameters being in good agreement with the data in other neutron-irradiated quartz samples. Therefore, in a first attempt to analyze the clathrate data, we have used the same modification with a cut off in the λ distribution. In terms of the parameters E and $u = (\Delta_0/E) = (\tau_m/\tau)^{1/2}$ used in the general expression (Eq. (2)) for the absorption, the λ restriction corresponds to changes of the lower integration limit in u (called $u_{\min}$). As mentioned above, the plateau appears when $\omega\tau = 1$, thus longer relaxation times (and smaller u values) are involved; therefore changes in the lower integration limit have to be considered to describe changes in the plateau.

As illustrated in Fig. 2, the data can be modeled quite well with the modified tunneling model: the calculated attenuation fits both the maximum and the frequency-independent T^3 at the lowest temperatures. Table 1 lists the TS-parameters derived from the fit, and, for comparison the parameters for typical glasses like SiO_2 and GeO_2. $(\tau_m/\tau)_{\min}$ represents the cut off of the λ-distribution. From K_3, a value for the coupling parameter γ can be calculated. This is done with the assumption $\gamma_l^2/v_t^2 = \gamma_l^2/v_t^2$, which is found to be valid for isotropic (amorphous) solids [15]. However, $Sr_8Ga_{16}Ge_{30}$ is not amorphous, and the above assumption might not be correct for this crystal. The calculated values for γ and $\bar{P}$ (derived from $\bar{P}\gamma_l^2$) should therefore be seen as a "first estimate" rather than an accurate value. C $(= \bar{P}\gamma_l^2/\rho v_l^2)$, and K_3 are derived directly from the fit, and are therefore reliable within the experimental accuracy of 10%. Comparing the values found for the crystal with those for glasses, we see that $\bar{P}\gamma_l^2$ is significantly lower in $Sr_8Ga_{16}Ge_{30}$ than in glasses. This is not a surprise: $Sr_8Ga_{16}Ge_{30}$ is a crystal and is not expected to show glasslike behavior at all. The values we find here are comparable to those found in electron-irradiated quartz [16], which is a slightly disordered (not amorphous) crystal.

Table 1
Tunneling parameters derived from the modified tunneling model, as described in the text

	$Sr_8Ga_{16}Ge_{30}$		a-SiO_2	a-GeO_2
	155 MHz	250 MHz		
C (10^{-6})	9.7	9.3	620	400
K_3 ($10^7\,K^{-3}\,s^{-1}$)	63	63	20	60
$\bar{P}\gamma_l^2$ ($10^6\,g\,cm^{-1}\,s^{-2}$)	11.0	10.4	450	190
$\bar{P}$ ($10^{30}\,erg^{-1}\,cm^{-3}$)	7.0	6.8	360	370
γ_l (eV)	0.77	0.77	0.70	0.45
$(\tau_m/\tau)_{\min}$	10^{-6}	10^{-6}	0	0

Both RUS and attenuation measurements show that $Sr_8Ga_{16}Ge_{30}$ is a fascinating crystal with unusual properties, behaving very much like an amorphous solid. An element of disorder present in $Sr_8Ga_{16}Ge_{30}$ is the random substitution of Ga for Ge; i.e., the Ga and Ge atoms appear to be fully disordered on the three distinct framework sites [10]. However, if this random substitution were to be the source of the tunneling states in $Sr_8Ga_{16}Ge_{30}$, the same glasslike behavior would be expected for similar clathrates. Thermal conductivity data for $Ba_8Ga_{16}Ge_{30}$ shows a crystalline temperature-dependence, with no evidence for tunneling states [13]. Both samples have the same clathrate structure, but structure refinements based on neutron scattering experiments have revealed a major difference between $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$: the atomic displacement parameter (ADP), which measures the mean-square displacement amplitude of an atom about its equilibrium position in a crystal, is anomalously high for one of the two Sr atoms in the $Sr_8Ga_{16}Si_{30}$ unit cell. The position of this Sr-atom is better described by a fractionally occupied fourfold split site. In $Ba_8Ga_{16}Ge_{30}$, the Ba-atom behaves 'normally', and can be refined with a single site model [17]. The significant differences between $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ provide strong evidence that the glasslike tunneling states in $Sr_8Ga_{16}Ge_{30}$ at low temperatures and the 2-level system at slightly higher temperatures have to be associated with the 'loose' Sr-atom, tunneling between its four possible equilibrium positions. Although the environment of the Sr-atom can be slightly different from site to site (e.g., the neighboring metal ions can be Ge or Ga), it is not as random as it would be in an

amorphous solid. The distribution of the tunnel parameters is therefore expected to be limited, which is consistent with the results from the attenuation measurements.

4. Summary and conclusions

RUS measurements in $Sr_8Ga_{16}Ge_{30}$ reveal the presence of a low-energy vibrational mode, with a characteristic energy of 45 K. Ultrasonic attenuation measurements show that the low temperature behavior ($T<1$ K) is dominated by tunneling states. The presence of glasslike tunneling states in a well-characterized crystal structure makes $Sr_8Ga_{16}Ge_{30}$ a unique material. Being one of only a few materials in which the tunneling states are identified, it opens new possibilities for investigating the low-energy excitations. So far, no evidence for glasslike excitations has been found in $Ba_8Ga_{16}Ge_{30}$. A systematic study of a series of clathrates, with carefully selected guest- and cage-atoms could help to determine the ideal conditions for inducing glasslike behavior in a crystalline environment.

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