Direct observation of resonant states associated with vacancy defects in the chalcogenide sublattice of PbTe

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A δ-function singularity has been observed in the state density of the conduction band in polycrystalline samples of n-type PbTe with a slight excess of lead ($\sim$0.1 at. %) by the method of low-temperature calorimetric spectroscopy. This singularity is interpreted as a narrow ($\sim$0.01-eV) band of resonant states associated with vacancy defects in the anionic sublattice of the samples.

1. A thorough low-temperature calorimetric study of a series of samples of n-type PbTe with electron densities over the range $n = 2\times10^{17}$–1.8×10^{20} cm^{-3} has been undertaken in order to make a detailed study of the behavior of the state density in the PbTe conduction band.

The samples had a polycrystalline structure and were synthesized by a metal-ceramic method. Iodine was selected as the dopant whose concentration was varied in order to vary the electron density (the Fermi level ϵ_F). The overwhelming majority of the test samples had the nominal composition $Pb_{1.002}Te_{1-x}I_x$.

2. An analysis of the results of the calorimetric measurements, which were taken over the interval 1–20 K with a relative error of 1–2% at $T<4$ K and with an error possibly larger by a factor of 3–5 up to 20 K, revealed that for all the samples studied, and at all the temperatures studied, most of the measured heat capacity C is the lattice component C_l, which at $T>5$–7 K is essentially the same as that for undoped PbTe, as published in Ref. 1. At low temperatures (1–2 K) we saw a decrease in C_l which became progressively more pronounced as the iodine concentration N_I was increased. This decrease reached 7–10% in comparison with the figure for undoped PbTe in the samples with the maximum values of N_I.

3. Original and nontrivial results were extracted from the experimental curves of $C(T)$ after the elimination of the term which depends linearly on the temperature, $C_n = \gamma T$ (the electron heat capacity).[2)] We know that for a statistically degenerate electron system with an energy spectrum which is quasicontinuous (in comparison with the experimental value of k_0T) the coefficient γ is the same, within an essentially constant factor, as the electron state density at the Fermi level, $g(\epsilon_F)$.

Figure 1 shows data on the dependence $\gamma(n)$ found from the experiments. The smooth part of the curve, which rises monotonically with increasing n, can naturally be linked with the density of band (propagating) states, which form the c band in PbTe. A comparison of this smooth calorimetric $\gamma(n)$ curve with the dashed line (see the note in the figure caption) confirms the data of many investigators[3] pointing to a pronouced deviation from a parabolic nature for the main band extrema in PbTe.

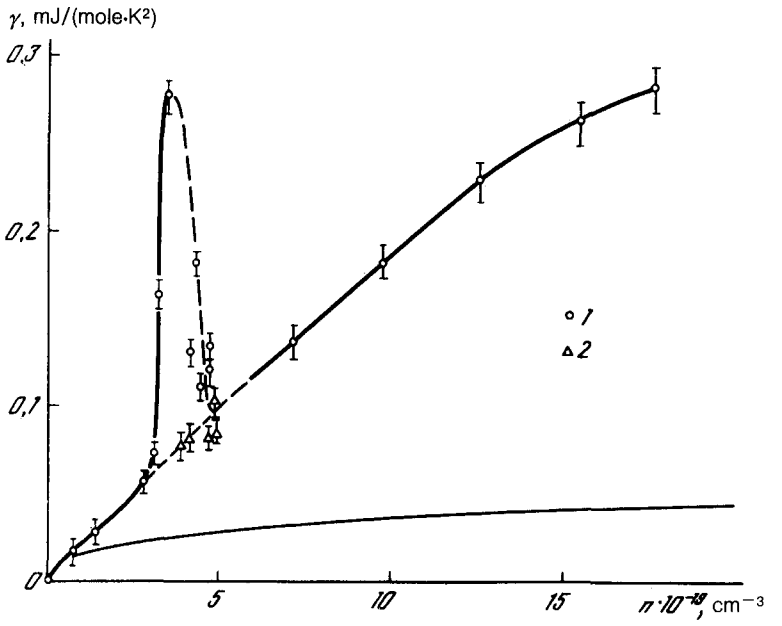

FIG. 1. The electron specific heat of the n-type PbTe⟨I⟩ samples studied versus the electron Hall density (300 K). 1—Samples annealed at 600 °C; 2—compositions annealed at 350 °C.
Note. The dashed line is the calculated $\gamma(n)$ dependence for a band with a quadratic dispersion law $\epsilon(\mathbf{k})$ with an effective state-density $m_d^* = 0.12m_0$ (Ref. 2).

4. The most remarkable features of the data in Fig. 1, however, is of course the sharp anomaly in $\gamma(n)$ near $n = 3.5\times 10^{19}$ cm^{-3}, in the form of a δ-function spike in the state density. At its peak the values of $g(\epsilon_F)$ are characteristic of samples with the highest electron densities which have been achieved for n-type PbTe⟨I⟩.

The comparatively small width of the feature observed in $\gamma(n)$, some 30–40 meV along the energy scale, indicates that this feature should be identified with a resonant level (or band) which is genetically related to defects of some sort in the lattice of the test samples.

The nature of the $\gamma(n)$ and $n(N_I)$ curves obviously rules out the possibility that the observed level can be associated with the iodine dopant (Ref. 4, for example).

On the other hand, the presence of an excess of lead in the samples—lead is customarily added in the metal-ceramic method for synthesizing n-type PbTe in order to improve its electrical properties—and the fact that the possible deviations of the compound PbTe from the exact stoichiometric composition could go in two directions[3] suggest that the resonant level observed in Fig. 1 is related to vacancy defects in the anionic sublattice of the samples.

5. This conclusion, combined with the data in Fig. 1, may be regarded as the first direct experimental confirmation of the results of the theoretical work (first reported in Ref. 5 and, later, in Ref. 6). According to these results vacancies in the chalcogen-

ide sublattice of IV–VI compounds lead to the appearance, against the background of the energy spectrum of the conduction band, of three resonant levels per vacancy.

Making use of this circumstance, and replotting $\gamma(n)$ as a curve of $g(\epsilon_F)$, we can easily integrate the δ-function spike above the monotonic (band) part of the $g(\epsilon_F)$ curve. As a result, we find the estimate $N_{V(\mathrm{Te})} \approx 8 \times 10^{18}$ cm^{-3} of the concentration of anion vacancies in our samples. This result seems to be a completely reasonable value for lead-rich metal-ceramic samples, and it agrees satisfactorily with existing data[3] on the solubility of lead in PbTe.

An estimate of the energy position of the resonant Te-vacancy level above the edge of the conduction band on the basis of data on the $\epsilon_F(n)$ dependence for PbTe at $T = 77$ K (Ref. 3) yields[3)] $E_{V(\mathrm{Te})} = 165 \pm 15$ meV.

6. The well-known multivaluedness of the experimental values near the resonant peak demonstrated by the experimental points in Fig. 1 is completely natural, in our opinion, and can be explained by several factors, which are apparently acting together: (a) the nonmonotonic change in the Hall coefficient (on the basis of which the values of n were determined) as ϵ_F passes through the region of the resonant peak, as has been found for a corresponding physical situation in PbTe⟨Tl⟩ (Ref. 7); (b) the manifestation of a fine structure in the resonant part of the integral $g(\epsilon_F)$ curve found experimentally; (c) the absence in principle from the test samples of a rigid coupling of n and $N_{V(\mathrm{Te})}$, which evidently determines the magnitude of the resonant increment in the band component of $g(\epsilon_F)$.

The latter circumstance provides a good opportunity for testing the conclusion reached above regarding the nature of the resonant level observed. Specifically, according to the data on the T–x phase diagram[3] of PbTe, the solubility of either Pb or Te in this compound decreases sharply with decreasing temperature. We would thus expect that samples which have been subjected to a comparatively low-temperature annealing ($T = 300$–400 °C) would not exhibit manifestations of a resonant increase in γ, despite the excess lead in their nominal composition—in agreement with experiment (Fig. 1).

The possibility of observing a peak of resonant states in the n-type PbTe samples is thus determined not only by their composition but also by their thermal history.

7. We conclude with a look at some results of measurements of the electrical properties of the test samples, which provide independent confirmation of the existence of this resonant level and which provide some important additional information on its properties.

Figure 2 shows data on the Hall mobility of the test samples of $T = 77$ K, supplemented with data published previously by one of the present authors for single-crystal and polycrystalline n-type PbTe samples.

It can be seen from Fig. 2 that the samples in the present experiments conform well to the typical curve of the Hall mobility[3] for n-type PbTe, except for three samples, which form a resonant spike in the state density in Fig. 1. For these samples, the values of $R\sigma$ are typically much lower. These low values are obviously evidence of an intense resonant scattering of electrons in the region $\epsilon_F \sim E_{V(\mathrm{Te})}$.

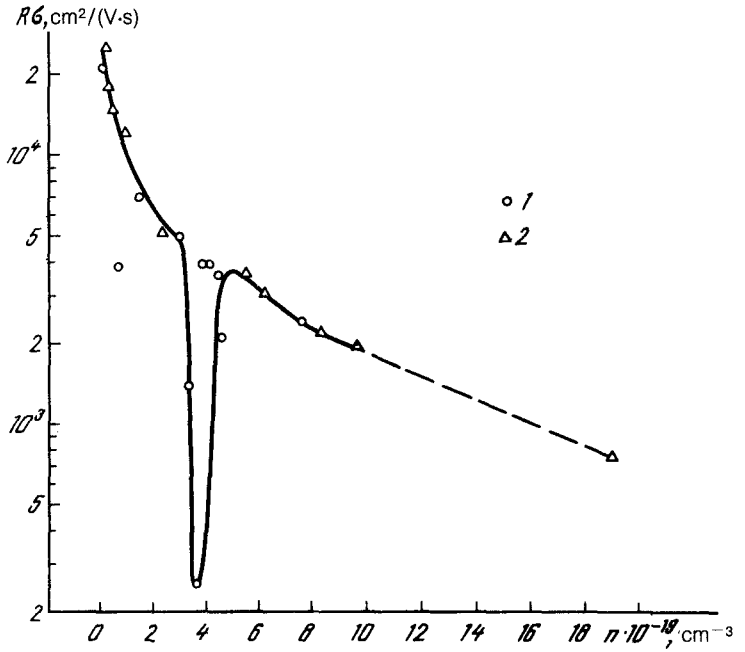

FIG. 2. The electron Hall mobility in n-type PbTe⟨I⟩ at 77 K. 1—The samples of the present study; 2—additional data borrowed from Ref. 2.

The results of preliminary measurements of $R\sigma$ at $T = 4.2$ K also reveal a rigid correlation between the resonant spike in γ and the dip (by more than an order of magnitude) in the value of $R\sigma$.

The presence of an intense resonant scattering of electrons in the samples is consistent with the following conclusions. (1) The properties of the Te-vacancy resonant levels, in terms of their interaction with the background band states, are quite different from the properties of the resonant states which are formed by indium in PbTe (Ref. 4) and are apparently similar to the resonant properties of thallium.[4,7] (2) The broadening of the Te-vacancy level to several tens of millielectron volts, which is observed experimentally, is caused primarily by factors related to a deviation from a quantum-mechanical stationary state.

The obvious similarity between the properties of n-type $Pb_{1+y}Te_{1-x}I_x$ and p-type PbTe⟨Tl⟩ (p-type $Pb_{1-x-y}Tl_xNa_yTe$) suggests that we could expect the possibility of a resonant defect superconductivity in the former material. This phenomenon (a new type of superconductors), observed comparatively recently,[7,8] consists of the possibility of imparting to originally nonsuperconducting materials (in particular, semiconductors) the ability to form a superconductivity state by adding corresponding defects which form resonant states with properties similar to those of resonant levels of thallium in PbTe and by an optimum doping which puts ϵ_F near the resonant-state peak.

Although the data reported in this letter show no sign of a superconductivity in these samples, even in the most promising composition, with $\epsilon_F \approx E_{V(\mathrm{Te})}$, they nevertheless do not rule out the possibility of a superconductivity transition with $T_c < 1$ K, which is, unfortunately, beyond our present technical capabilities.

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[2)]For the samples with the maximum values of γ, the ratio C_n/C_l is 0.25–0.3 at $T = 1$ K.
[3)]This estimate should apparently be corrected in the direction of an increase in $E_{V(\mathrm{Te})}$ because of the difference in the temperatures of our calorimetric data (1–2 K) and the dependence $\epsilon_F(n)$ borrowed from Ref. 3, which was actually recorded at $T \approx 80$–90 K.

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