

Kondo effect in IV-VI semiconductors with noncentral ions

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A logarithmic temperature dependence of the resistance, $\rho(T)$, has been observed in $\text{PbTe}_{1-x}\text{S}_x$ compounds. This temperature dependence is suppressed by an electric field. The $\rho(T)$ anomaly stems from a scattering of electrons by two-level centers: noncentral S^{2-} ions. This anomaly is sensitive to the presence of an ordering of dipoles.

Ferroelectric phase transitions in crystals with noncentral ions are presently the subject of active research (see the review by Vugmeister and Glinchuk¹). In addition to the well-known semiconductor compounds $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ in which the noncentral ion is¹ Ge^{2+} , an anionic substitution compound, $\text{PbTe}_{1-x}\text{S}_x$, has recently been synthesized. This new compound demonstrates a ferroelectric phase transition due to a noncentral S^{2-} anion.³ So far, the resistance $\rho(T)$ near the critical temperature T_c (Ref. 3) and the Shubnikov oscillations at $T < T_c$ (Ref. 4) have been studied in $\text{PbTe}_{1-x}\text{S}_x$.

Since the compounds PbGeTe and PbTeS , being narrow-gap semiconductors with ferroelectric phase transitions caused by noncentral ions, are somewhat similar in

terms of their properties, one can expect in the new compound PbTeS an anomaly in the resistance corresponding to that in PbGeTe . The anomaly consists of the presence of a minimum and of a logarithmic growth of the resistance as the temperature is lowered in the liquid-helium region.^{5,6} The anomaly stems from a scattering of particles by Ge^{2+} ions, which constitute two-level centers or dipoles which undergo a tunneling along one of the $\langle 111 \rangle$ axes.

In this letter we report measurements of $\rho(T)$ in $\text{PbTe}_{1-x}\text{S}_x$ single crystals and $\text{Pb}_{1-x}\text{Ge}_x\text{Te}$ films; we report the first observation of an effect of the Kondo type in $\text{PbTe}_{1-x}\text{S}_x$ compounds; and we also report a study of the effect of an electric field on this Kondo effect.

The experiments were carried out by a four-probe method on $\text{PbTe}_{1-x}\text{S}_x$ single crystals ($x = 0.05$, $n = 1.8 \times 10^{17} \text{ cm}^{-3}$; $x = 0.08$, $n = 6.5 \times 10^{17} \text{ cm}^{-3}$), cut in the form of parallelepipeds with dimensions of $6 \times 2 \times 1 \text{ mm}$, and a $\text{Pb}_{0.96}\text{Ge}_{0.04}\text{Te}$ film with a carrier density $n = 8 \times 10^{16} \text{ cm}^{-3}$, deposited on cleaved BaF_2 . The compositions of the single crystals were determined within 10^{-3} from the $T_c(x)$ dependence.³ The composition of the films was set by the ratios of components in the stock material and was monitored by an optical method on the basis of the position of the optical absorption edge. The error in the determination of the changes in ρ with respect to its values at $T = 4.3 \text{ K}$ was 1%.

Figure 1 shows the results of measurements of $\rho(T)$ of the $\text{PbTe}_{1-x}\text{S}_x$ single crystals. A linear dependence $\rho(\ln T)$, characteristic of the Kondo effect, was observed without magnetic impurities, as evidenced by the positive magnetoresistance and the absence of anomalies in the magnetic susceptibility. Over the temperature interval 4.3–40 K the Hall coefficient exhibits no anomalies and is essentially independent of the temperature (within 10%).

Fixing the predominant direction of the impurity dipoles with an electric field should suppress the scattering of particles accompanied by a change in the direction of the dipole, just as a magnetic field suppresses the Kondo effect in crystals with magnetic impurities. In order to produce a significant electric field in a sample with a high dielectric constant (10^3 – 10^4), we passed a current through the sample. In the case of

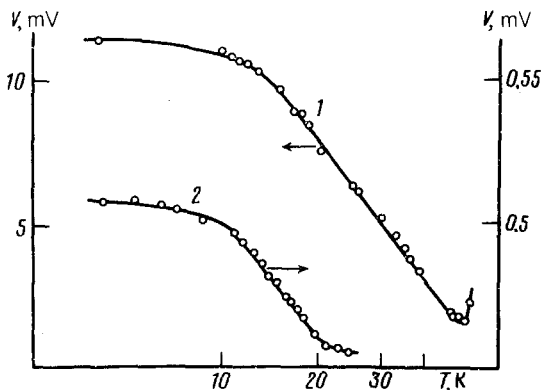


FIG. 1. Temperature dependence of the voltage drop across the probe contacts on $\text{PbTe}_{1-x}\text{S}_x$ single crystals. 1— $x = 0.05$; 2— 0.08 .

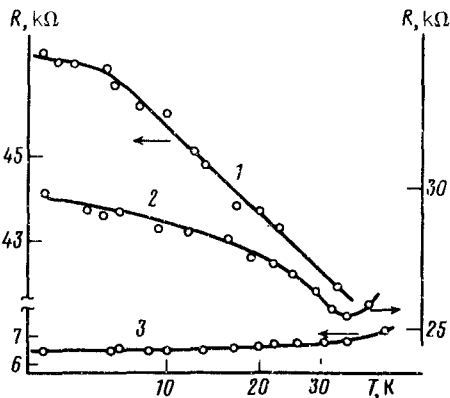


FIG. 2. Temperature dependence of the resistance of the probe contacts on $\text{Pb}_{0.96}\text{Ge}_{0.04}\text{Te}$ films ($n = 8 \times 10^{16} \text{ cm}^{-3}$) at various strengths of the electric field E : 1— $E \approx 0.4$; 2— 0.9 ; 3— 20 V/cm .

$\text{Pb}_{0.96}\text{Ge}_{0.04}\text{Te}$, the sample was a film and thus had a higher resistance than a single crystal of the same composition. Figure 2 shows plots of $\rho(\ln T)$ for various values of the current density (for various electric fields E). As E is increased, the first change is the disappearance of the linear part of the dependence; then the resistance minimum, in general, disappears.

A nonohmic behavior due to carrier heating is observed in PbTe only in fields $E \sim 10^3 \text{ V/cm}$. We measured current-voltage characteristics of the test samples. In the PbGeTe films in fields in the range $20\text{--}100 \text{ V/cm}$, for example, where the resistance anomaly discussed above has already been suppressed, the current-voltage characteristic is ohmic. This behavior is evidence that there is no deviation from an ohmic behavior due to heating effects in the weak fields which we used.

We observed the anomaly in $\rho(T)$ in only a limited interval of the composition x . The reason for the lower limit on x was a trivial one: the manifestation of a logarithmic part of $\rho(T)$, proportional to x . In order to understand the reason for the upper limit, we need to take into consideration the circumstance that in an ordered phase [it was in an ordered phase that $\rho(T)$ was measured] there is an infinite cluster of noncentral ions (a ferroelectric or glassy cluster). As the composition x is increased, the relative number of ions which are not part of this infinite cluster decreases. Specifically, these individual centers or small clusters are effective scatterers in this case, since the directions of their dipole moments are not fixed by the interaction with dipoles belonging to the infinite cluster.

¹The first experimental proof that the Ge^{2+} ion is a noncentral ion in PbTe was recently found by Islam and Bunker.²

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