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NEGATIVE PHOTOCONDUCTIVITY AND LARGE LATTICE RELAXATION IN INDIUM DOPED LEAD - TIN - TELLURIDE

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We report a low-temperature negative photoconductivity in lead-tin-telluride doped with indium. This negative photoconductivity is unusual in that it is the first such effect reported in a narrow-gap semiconductor, the first reported in strongly p-type material, the fastest yet observed, and occurs only below a sharp transition temperature of 21 K. A model is proposed which involves electronic transitions between various charge states of indium, resulting in large lattice relaxation. The same model can also explain other recently reported low-temperature transport anomalies in lead-tin-telluride.

I. Introduction

Doping of lead-tin-telluride ($Pb_{1-x}Sn_xTe$, or LTT for short) with indium leads to electrical properties which can be varied from degenerate "metallic" to "semi-insulating" by variation of composition x, temperature, pressure, and concentration of dopants. It has thus been the subject of much recent attention.

We have observed an unusual negative-photoconductivity (NPC) in LTT (x=0.25) doped with indium. NPC, although fairly rare, has been found in several large-gap n-type materials partially compensated with multiple-charge-state deep level impurities; this is now fairly well understood in terms of a model in which photo-excited holes produce a weak increase in conductivity, but are then rapidly trapped, leading to a longer-term trapping of conduction electrons and a consequent net decrease in conductivity [1,2]. The NPC observed until now has always been slow (typical time constants of seconds, the fastest being milliseconds [1]) and usually seen only close to room temperature. By contrast, the NPC reported here is observed for the first time in a strongly p-type narrow-bandgap semiconductor, is rather fast, and occurs only below a very sharp transition temperature of only 21 K.

II. Experimental Results

Samples were high quality crystalline films [3] (about 4 μm thick) grown on BaF_2 substrates. The substrate was mounted onto the copper cold-finger of a variable temperature cryostat. Figure (1) illustrates the temperature dependence of the dark resistance and photoconductivity of a p-type LTT sample with x = 0.25; the sample is similar in electrical properties to sample (c) of [3]. (Our Fig. (2) is a reproduction of Fig. (2c) of [3].)

The main curves in Fig. (1) show the dark resistance R and the change in resistance ΔR under illumination with a low intensity 10.6 μm line from a CO_2 laser. The solid curve of the insert shows the time response of the NPC (photo-induced increase in resistance) at a temperature of 7 K. (Note: The actual sample temperature may be slightly higher than indicated, due to the physical separation between the thin film sample and the thermometer which is mounted onto the copper cold finger. However, measurements of R and ΔR were recorded

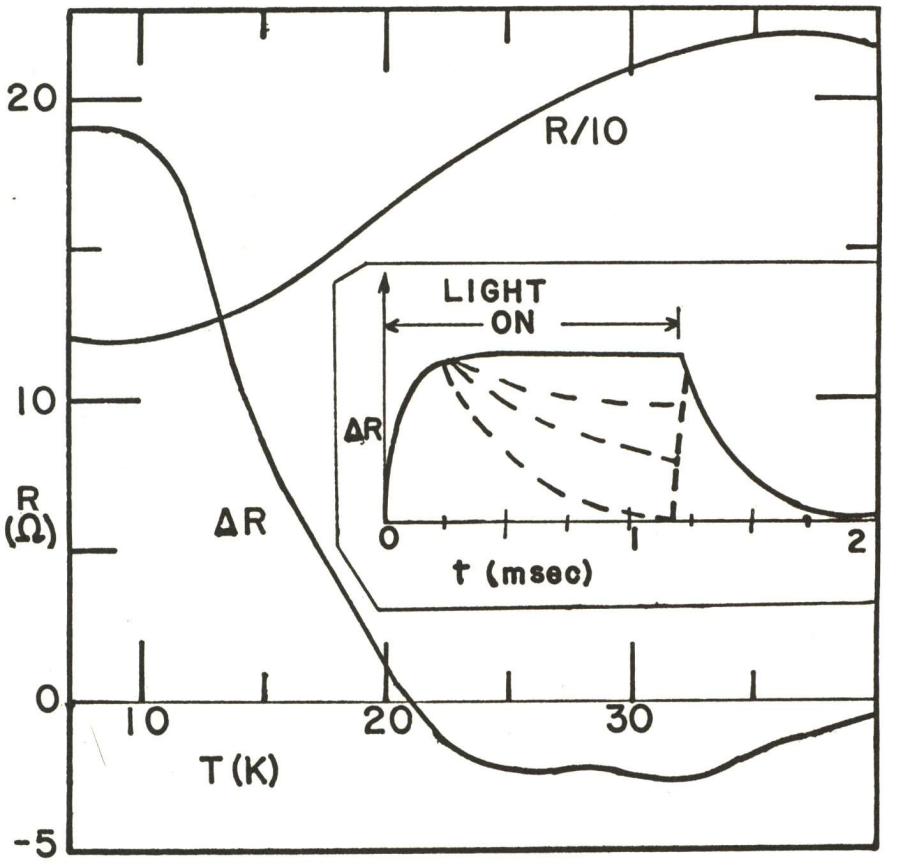

Fig. (1) Dark resistance and photoconductivity of p-type $Pb_{0.75}Sn_{0.25}Te$:In with In concentration in middle $10^{18}/cm^3$ range

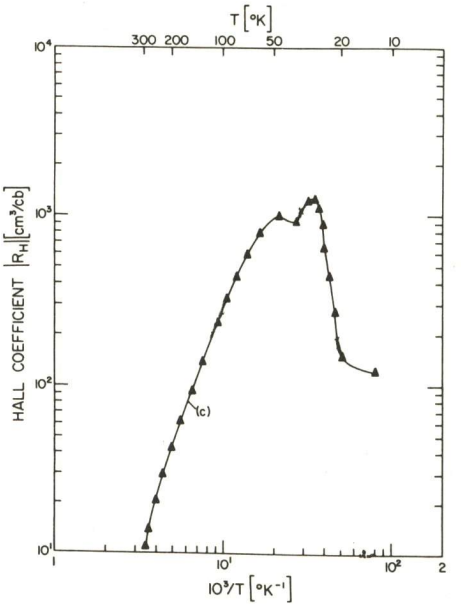

Fig. (2) Hall coefficient of sample (c), x = 0.25 reproduced from [3]

simultaneously, and thus correspond to identical sample temperatures.)

The decay time of the NPC when the light is turned off is about 200 μsec. The rise time when the light is turned on is observed as about 100 μsec, but is presumably faster, as this is approximately the rise time of the light intensity due to the limited speed of the mechanical chopper. As the temperature is increased, the time response remains essentially constant, but the photosignal decreases in magnitude, crossing zero at about 21 K and then changing to a weak ordinary photoconductivity (photoinduced decrease in resistance), whose decay time is about 100 μsec and rise time about 200 μsec. The transition temperature of 21 K is quite sharp, independent of incident light intensity, independent of whether the temperature is rising or falling, and shows no hysteresis effects. The negative photoconductivity (below 21 K) signal level increases approximately as the square root of the incident photon flux, whereas the normal photoconductivity (above 21 K) signal level increases approximately linearly with the incident photon flux.

For large incident light intensities (above 0.6 watts peak) an unusual saturation effect begins to occur, as indicated by the dotted curves of the inset in Fig. (1). The lowest of these dotted curves corresponds to a peak incident power of 1 watt. Although it has a turn-on time of about 500 μsec and a turn-off time of about 100 μsec for steady state chopped light, it appears slowly with a time constant of about 0.7 seconds when the light is initially turned on with an additional shutter. This is indicated schematically by the succession of dotted curves moving from the top down. This unusual saturation effect will be discussed elsewhere [4]; it is not observed in the normal photoconductivity above 21 K.

III. Discussion

The temperature dependence of the Hall coefficient for LTT:In for various alloy compositions x, has been explained [3] in terms of an "autocompensation" model in which neutral indium, In°, is unstable, and decays spontaneously by the process

$$2In^{\circ} \rightarrow In^{+} + In^{-} \qquad (1)$$

because of a negative correlation U [5]. Such a model has been called an "Anderson negative U" model [6] and is a consequence of large lattice relaxation around the In impurity. The Fermi energy in such a system tends to be pinned between the In^{+} donor level and the In^{-} acceptor level. (See [6] for discussion of the meaning of "level" in such a system.) As the bandgap of LTT decreases with decreasing temperature [7] ($dE_g/dT = 0.46$ meV/K), at about 21 K the valence band edge crosses the In^{-} level, and almost all the In converts to In^{-}. This produces a rapid increase in the number of valence holes, which then remains constant as the temperature is lowered further [3], thus explaining the behaviour of the Hall coefficient in Fig. (2). The situation below 21 K is illustrated in Fig. (3) by a configuration-coordinate-like diagram similar to the total energy functional curves of [6].

The NPC below 21 K can be explained with reference to the dotted arrows of Fig. (2), and the "reactions" indicated below.

$$2p + In^{-} \xrightarrow{\text{optical absorption}} 2p + e + In^{\circ} \qquad (2)$$

$$2p + e + In^{\circ} \xrightarrow{\text{electron hole recombination}} p + In^{\circ} \qquad (3)$$

$$p + In^{\circ} \xrightarrow{\text{hole capture}} In^{+} \qquad (4)$$

Process (3) is rapid due to strong direct electron-hole recombination in LTT; (4) should be rapid because the sample is degenerate p-type below 21 K. The thermal emission of holes from In^{+} to return the system to equilibrium in the

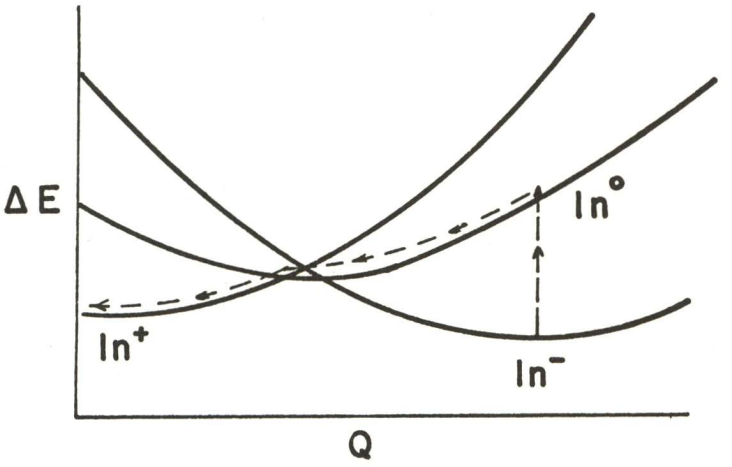

Fig. (3)

dark, should be slower because of the thermal activation energy required for emission of the first hole. Direct band-to-band absorption should produce a very weak competing ordinary photoconductivity due to the short lifetime of the minority electron. Hole emission by In° would compete with process (3), but is presumably slower in the degenerate p-type material below 21 K.

IV. Conclusions

The negative correlation energy U of In in LTT has been used to explain the anomalous behaviour of the Hall coefficient [3]; its implied large lattice relaxation has explained the low-temperature negative photoconductivity, and can also explain [4] persistent photoconductivity observed in n-type LTT highly doped with In [8]. The negative U and large lattice relaxation indicate that the In impurity states are much more highly localized than one would at first suspect from the low binding energies in narrow gap semiconductors.

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VI. Footnotes and References

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1) M.C.P. Chang, C.M. Penchina & J.S. Moore; Phys. Rev. B4, 1229 (1979) and refs. C.M. Penchina, J.S. Moore & N. Holonyak Jr.: Phys. Rev. 143, 634 (1966)
2) R.H. Bube. "Photoconductivity of Solids", John Wiley, NY (1960)
3) K. Weiser, A. Klein and M. Ainhorn: Appl. Phys. Lett. 34, 607 (1979)
4) C.M. Penchina et al. (to be published)
5) P.W. Anderson: Phys. Rev. Lett. 34, 953 (1975)
6) G.A. Baraff, E.O. Kane and M. Schluter: Phys. Rev. to be published (1980)
7) A.J. Strauss: Trans. Metal. Soc. AIME 242, 354 (1968)
8) B.M. Vul et al.: JETP Lett. 29, 18 (1979)