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ELECTRICAL TRANSPORT MEASUREMENTS IN TiS_3

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Results of measurements of conductivity and Hall coefficient in the temperature range 15-300K and of thermal emf in the temperature range 80-400K, carried out on TiS_3 samples, are reported.

The results indicate that these crystals are semiconducting with extrinsic n-type conductivity. The mobility of the carriers is about 30 cm^2/V sec at room temperature, increases up to about 100 cm^2/V sec at 100K and drops at lower temperatures. The Seebeck coefficient is in qualitative agreement with these findings but its detailed temperature dependence is not yet understood.

Introduction

TiS_3 belongs to the group IV transition metal trichalcogenides. This group[1,2], like the group V trichalcogenides crystalizes in a chain structure of trigonal prisms with the metal ion occupying the centers of the prisms. In contrast to the group V compounds the detailed structure of the group IV compounds is simpler consisting of a single type of chains and a unit cell containing only two formula units. The structure indicates[3] that MX_3 is effectively $M^{4+}X^{2-}X_2^{2-}$ thus having an empty d band.

Electrical, optical and crystallographic properties of TiS_3 have been investigated[4,5] already more than twenty years ago. It was shown[4] that it is a semiconductor with a gap of about 0.9 eV and that its n-type conductivity is governed by two donor levels located ∿ 0.06 eV and 0.14 eV below the conduction band. The relative role of the two types of donors was found dependent on the heat treatment of the crystals. The above values were estimated from the slopes of linear portions of $\ell n\, \sigma$ versus the reciprocal temperature observed for various samples below 200K. The common feature of all such plots for various TiS_3 samples shown in Ref. 4 is the occurrence of a maximum in the conductivity above 200K. Such maximum could a priori be attributed to the competition of the opposite dependences on temperature of the carrier concentration and the mobility. However, it is probably the resemblance of this maximum with that occurring in the conductivity of TaS_3 that triggered a renewed interest[6,7] in TiS_3 . TaS_3 like $NbSe_3$ exhibits spectacular phenomena of Peierls transitions and electronic instabilities associated with sliding charge density waves. The value of its maximal conductivity which occurs above the Peierls transition is orders of magnitudes higher than the range of values it obtains in TiS_3 and it may be that the resemblance of the maxima in the two materials is accidental. However, it is the apparent simplicity of TiS_3 that turns it into an attractive quasi-one-dimensional system for the study of transport properties. Hall measurments are difficult in the semiconductors with chain-like structure due to the small cross-section of the samples. Such measurements reported in the literature[8] were done only on ZrS_3 single crystals. In this communication we report on measurements of conductivity, Hall and thermal emf carried out on TiS_3 single crystals, in a large range of temperatures.

Experimental Results and Discussions.

TiS_3 single crystals were grown from a mixture of its constituents with excess sulfur (1:4) in evacuated quartz tubes in a temperature gradient 500-550 C for three weeks. Samples with typical dimensions of 5×0.1×0.005 mm^3 were used for four probe conductivity and Hall effect measurements. The thickness of these samples is comparable to that of the ZnS_3 samples[8] but their width is smaller by a factor of ten. Therefore the major difficulty encountered in this work was the application of side contacts to the samples. Several methods were used but only the following gave satisfactory results. Thin gold wires were attached to the samples with gold filled epoxy. To prevent contamination of the samples the heat treatment required by the epoxy was done at a relatively low temperature (100C). The Hall effect measurements were done in a helium cooled cryostat in the range of temperatures 15-300K and in magnetic fields up to 6 KG. The magnetic field was normal to the wide faces of the samples, The Hall and longitudinal voltage drop in two out of five samples we succeeded to prepare by the method described above were very noisy. In the other three it was reasonably clean and reproducible. The results obtained in these three samples will be discussed below.

The thermoelectric measurements combined with two probe conductivity measurements were done in a separate nitrogen cooled cryostat in which the temperature could be raised up to 500K. The samples for this type of measurements bridged two separate copper heat sinks. Their ends were inserted in grooves in the copper blocks and covered by silver paint or indium amalgam. Auxiliary experiments in a separate sample holder for four probe conductivity measurements showed that these contacts were ohmic and of negligible resistance when they surrounded the samples. No effect of the contacts was found in the temperature dependence of the thermal emf. Mechanical damage introduced by handling caused a significant reduction in the measured emf. It was also found that above 400K the results become irreproducible. The heat treatment increased the resistance of the samples and decreased their thermal emf at all temperatures. Microscopic inspection of such samples shows that they lost luster and became fibrous.

The results of the conductivity and Hall measurements are represented in Figs. 1 and 2. The data were interpreted in terms of a single type of carriers. Therefore the carrier concentration in Fig. 1b and Fig. 2 (on an expanded temperature scale) represents $(eR)^{-1}$ where e is the electronic charge and R - the measured Hall coefficient; the Hall mobility in Fig. 1c represents the product σR. The estimated error in the data introduced by the finite size of the contacts and the uncertainty in the measurements of the thickness of the samples is about a factor of two. The noise in the data increases with decreasing temperatures and is due to the small size of the potential probes. As mentioned above the quality of the four probe and two probe conductivity is greatly improved when larger probes can be used. Therefore the differences between the data of the three samples can be regarded as spurious except for the low temperature regime. The room temperature conductivity of our samples is about one order of magnitude larger than that reported in Refs. 4, 6 and 7. The temperature dependence of σ has features similar to those seen in Fig. 1 of Ref. 7 in the corresponding temperature range but in our samples the maximal conductivity is shifted to higher temperatures.

The Hall coefficient is n-type at all temperatures. As seen in Fig. 2 the room temperature carrier concentration $n(RT) \approx 5 \pm 3\times10^{18}$ cm^{-3}. The weak dependence on temperature close to this point indicates the approach to the exhaustion regime. An activation energy can be determined in the temperature range 80-200K. It corresponds to a donor level located 80 ± 5 meV below the conduction band. The effect of the weak temperature dependence of the effective density of states is less than the error bar. The extrapolated value of n from the linear portion of this graph to $T^{-1} = 0$ gives $8\times10^{19} > n_\infty > 2\times10^{19}$ cm^{-3}. This result sets an upper limit to the effective density of states - N_C of the conduction band in this range of temperatures. That is, while the donor concentration $N_D \geq n(RT)$ and $n_\infty = (\frac{1}{2} N_D N_C)^{1/2}$ then $N_C \leq 2\times10^{20}$ cm^{-3}. This limit is small compared to the concentration of TiS_3 molecules in the crystals ($= 1.36\times10^{22}$ cm^{-3}). It indicates that the conduction band is wide compared to kT and and also that the effective mass of the carriers

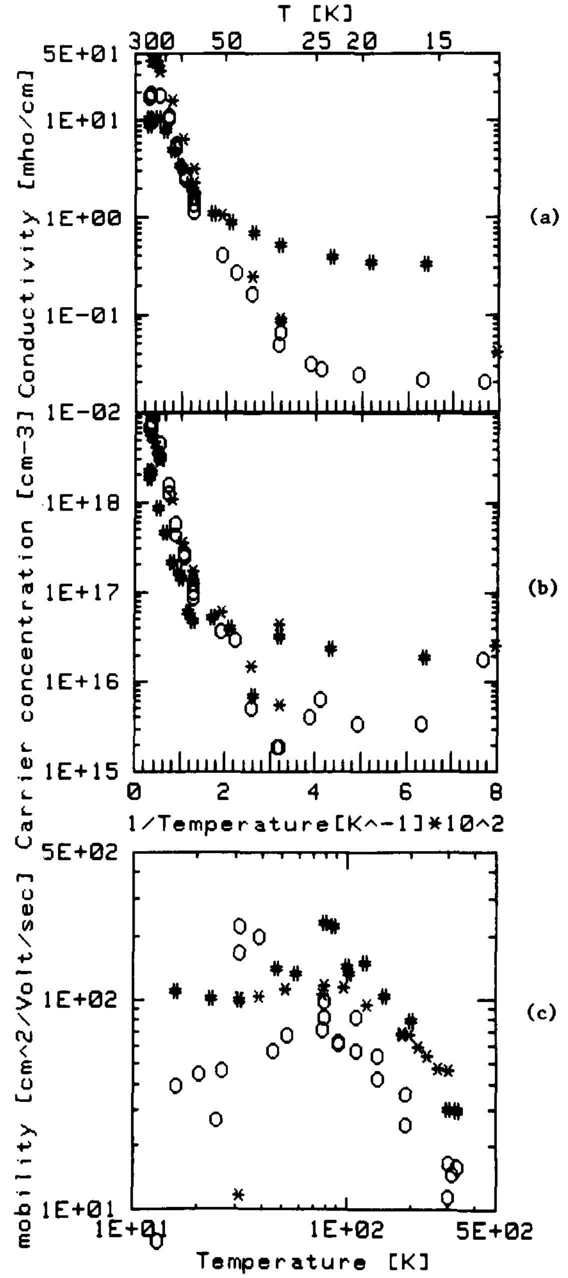

Fig. 1. Conductivity (a) and carrier concentration (b) plotted vs. 100/T and Hall mobility (c) plotted vs. T for TiS_3 samples.

Various symbols represent different samples.

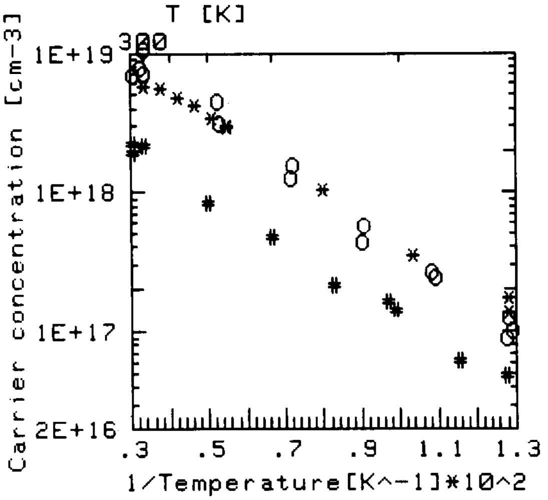

Fig. 2. Carrier concentration of TiS$_3$ samples above 80 K samples plotted vs. 100/T on an expanded scale.

is smaller than the electronic mass. The temperature dependence of n at temperatures below 80 K becomes weaker. This may be due to excitation of carriers from shallower levels. In this context we would like to make the following remark. In a sample of TiS$_3$ of 5 μm thickness there are 10^{-4} surface molecules for each bulk molecule. This number indicates therefore that the surface may act as a major source of free carriers in the bulk.

The Hall mobility (Fig. 1c) is plotted as in Ref. 8 for ZnS$_3$. Its room temperature value for the three samples is about 30 cm^2/V sec. It is comparable to that measured in the ZnS$_3$ samples, It increases with decreasing temperatures, passes a maximum and drops. A similar tendency is observed in the behavior of the mobility of the carriers in ZnS$_3$, though the measurements there extend only down to 100 K. The results in ZnS$_3$ were interpreted in terms of phonon scattering which dominates at high temperatures and ionized impurity scattering which dominates at low temperatures. The expression for the mobility used by them implies an isothropic medium and a concentration of ionized impurities which is independent on temperature, both assumptions being inadequate.

Fig. 3a represents the Seebeck coefficient - S of TiS$_3$ samples plotted vs. T^{-1} . The semi-log plot of the conductivity vs. T^{-1} measured in situ is shown in Fig. 3b. S is negative and increases with decreasing temperatures. The diffusion thermal emf for a single type of carriers and a single type of scattering is given by:

$$S = (k/e)[\ln(N_C/n) + A]$$

where k is the Boltzman constant and A is the so called heat of transport. When the relaxation time approximation is valid and the energy dependence of the relaxation time is of the type E^s then A is temperature independent and is of the order of several units. The value of A for impurity scattering is larger than that for phonon scattering. Therefore, for constant A, the slope of S vs 1/T yields in principle an activation energy equal to that of the carrier concentration. From Fig. 3 we see that the apparent slope of S vs. 1/T yields an activation energy which is almost twice the activation energy found from the conductivity (which is practically that of the carrier concentration) in the same range of temperatures. The plot of S vs. T^{-1} found in ZnS$_3$ exhibits also a deviation from the slope dictated by the carrier concentration, though less severe than in our case. It was attributed there to the gradual increase of A with decreasing temperatures, caused by the competition of two scattering mechanisms. The true source of the excess slope requires careful examination, both experimental and theoretical. This is an important issue because a similar effect was recently[10] found in the semiconducting phase of TaS$_3$. There the slope of S vs. T^{-1} yields an activation energy larger by a factor of 3 than that estimated from the temperature dependence of the conductivity. Hall effect data are not yet available in TaS$_3$.

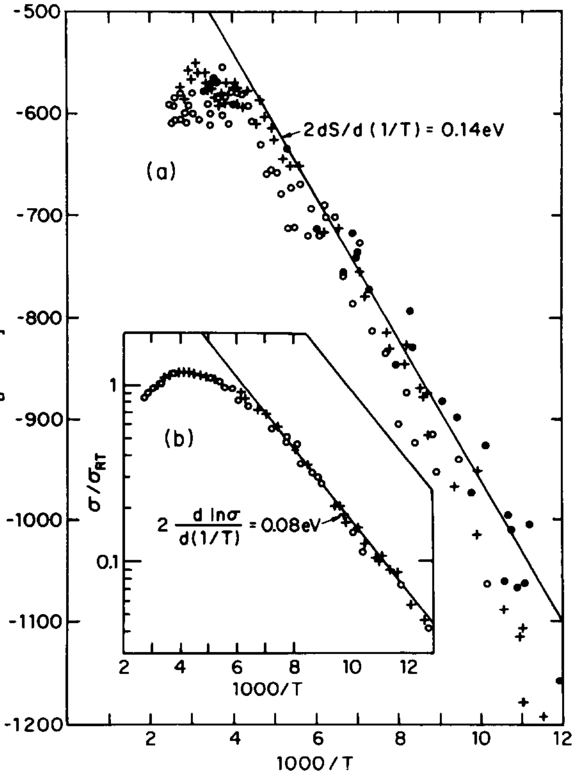

Fig. 3. Seebeck coefficient of TiS$_3$ samples plotted vs. 1000/T (a). Two lead resistance plotted vs. 1000/T (b) for the same samples.

Results of thermal emf measurements carried out on TiS_3 and ranging to lower temperatures than ours have been reported in Ref. 7. The larger value of S measured by them at room temperature indicates a lower carrier concentration. The temperature dependence of S in that work in the range of temperature overlapping that of ours is very different from that shown in Fig. 3. We cannot offer an explanation for the difference in the two sets of data.

Guided by the results reported in Ref. 4 we plan to vary the growth conditions of TiS_3 thus varying the electrical properties of the samples. It seems that a similar investigation carried out on additional members of the group IV transition metal trichalcogenides can be rewarding.

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