PHYSICAL REVIEW B VOLUME 36, NUMBER 8 15 SEPTEMBER 1987-I

Phonon-drag effect in $TiSe_{2-x}S_x$ mixed compounds

J. -M. Lopez-Castillo
Groupe du Conseil de Recherches Médicales du Canada en Sciences des Radiations, Université de Sherbrooke, Sherbrooke, Québec, Canada J1H 5N4 and Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Service des Basses Températures, 85X, 38041 Grenoble Cédex, France

A. Amara and S. Jandl
Groupe de Recherche sur les Semiconducteurs et les Diélectriques et Centre de Recherche en Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

J.-P. Jay-Gerin
Groupe du Conseil de Recherches Médicales du Canada en Sciences de Radiations, Université de Sherbrooke, Sherbrooke, Québec, Canada J1H 5N4 and Centre de Recherche en Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

C. Ayache
Centre d'Etudes Nucléaires de Grenoble, Département de Recherche Fondamentale, Service des Basses Températures, 85X, 38041 Grenoble Cédex, France

M. J. Aubin
Groupe de Recherche sur les Semiconducteurs et les Diélectriques et Centre de Recherche en Physique du Solide, Université de Sherbrooke, Sherbrooke, Québec, Canada J1K 2R1

(Received 3 April 1987)

Thermoelectric power (TEP) measurements of $TiSe_{2-x}S_x$ solid solutions have been performed in the temperature range 10–315 K for $0 \lesssim x < 2$. A phonon-drag effect is identified around 25 K. Its contribution to the TEP has been analyzed as a function of x. An estimate of the electron-phonon relaxation time $\tau_{e\text{-ph}}$ is derived from this analysis. This estimate is found to be in accordance with the value of $\tau_{e\text{-ph}}$ obtained from theoretical predictions.

I. INTRODUCTION

In a previous work,[1] thermoelectric power (TEP) measurements of $TiSe_{2-x}S_x$ mixed crystals were reported. The observed dip around 150 K in the alloys where the charge-density-wave phase transition is present was attributed to a phonon-drag effect due to a strong Γ-L interpocket electron-phonon interaction.

In the present study, additional measurements of the TEP of these materials are reported. A larger range of x values is investigated with an improved accuracy in the experimental measurements. Moreover, a better crystal-growing process is used, leading to more-stoichiometric materials. Our analysis is mainly focused on the low-temperature region below 100 K where we establish the evidence for an intrapocket phonon-drag effect near 25 K. Such a possibility was previously suggested in $TiSe_2$ by DiSalvo *et al.*,[2] and in $V_xTi_{1-x}Se_2$ and $Zr_xTi_{1-x}Se_2$ solid solutions by Gaby *et al.*[3]

II. EXPERIMENTAL RESULTS

We used iodine-vapor transport to grow homogeneous single-crystal samples of $TiSe_{2-x}S_x$, the high and low temperatures of the gradient being 740 and 640 °C, respectively. The lattice parameters of the obtained crystals were checked by x-ray diffraction. In the case of the $TiSe_2$ samples, the characteristic electrical resistivity ratio was $\rho(160\ K)/\rho(300\ K) \sim 3.2$. Typically, the dimensions of our samples were 5 mm long, 1 mm wide, and 0.05 mm thick. Electrical as well as thermal contacts were obtained with the aid of silver paint. The samples were mounted across the width on gold wires of 0.25 mm diameter. The gold wires were in good thermal contact with two copper blocks. Each of the blocks had a wound-wire heater which was used to establish a temperature gradient of less than 1 K along the sample. At each temperature, plots of thermoelectric voltage versus the temperature difference as measured by a differential Chromel–gold–0.07 at. % Fe thermocouple were made. The TEP was deduced from the slope of such plots, hence eliminating any contribution from stray voltages. Simultaneously, resistivity ρ and Hall coefficient R_H measurements were also carried out. The whole experimental process was computer controlled.[4]

Figure 1 shows the measured electrical resistivities of several $TiSe_{2-x}S_x$ samples. The large resistivity anomaly observed in pure $TiSe_2$ decreases gradually, as well as the transition temperature, when the sulfur concentration is increased. This resistivity behavior confirms the previously reported measurements of DiSalvo *et al.*,[2] and is qualitatively similar to the one observed in $Ta_xTi_{1-x}Se_2$,[5]

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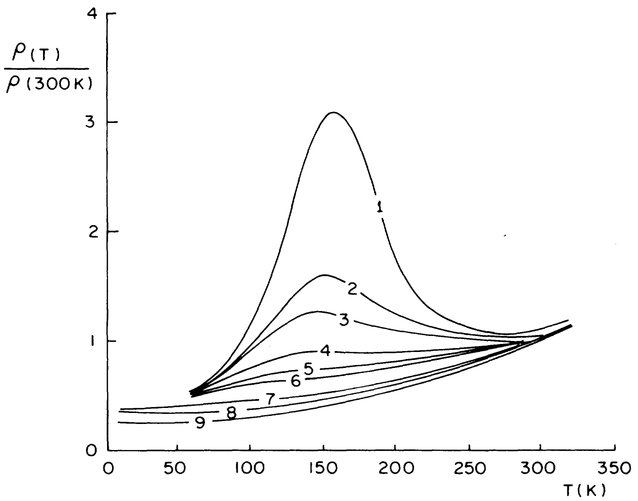

FIG. 1. Temperature dependence of the electrical resistivity ρ (perpendicular to the c axis) for $TiSe_{2-x}S_x$ single crystals. The values of x are as follows: 0 (curve 1), 0.2 (curve 2), 0.3 (curve 3), 0.4 (curve 4), 0.5 (curve 5), 0.6 (curve 6), 0.7 (curve 7), 0.8 (curve 8), and 1.0 (curve 9).

$Hf_xTi_{1-x}Se_2$,[6] and $Zr_xTi_{1-x}Se_2$.[7] It should be noted that, in contrast to these latter solid solutions where the transition disappears for very small x values, in $TiSe_{2-x}S_x$ the transition is still observed for x as large as 0.7.

In Fig. 2, Hall coefficient measurements of several $TiSe_{2-x}S_x$ samples with $x=0$, 0.2, 0.3, and 0.4 in the temperature range from 10 to 300 K are presented. As expected, the low-temperature residual electron concentration increases with the sulfur concentration. When sulfur is added, the temperature variation of the Hall coefficient becomes less pronounced and extends over a larger temperature range. In particular, R_H reaches a constant value at lower temperatures.

TEP measurements of investigated samples are shown in Fig. 3. Several remarks should be made. First, the invariant magnitude and position of the dip observed around 150 K in all transforming crystals support with strong evidence the previous findings of Lakhani *et al.*[1] Second, the good quality of our $TiSe_2$ sample is reflected in the fact that the TEP changes its sign at temperatures as low as 270 K, since deviations from stoichiometry would increase the electron concentration at the expense of the hole concentration.[2] Finally, the addition of increasing amounts of sulfur gradually reduces the broad plateau observed in $TiSe_2$ below 100 K. In this work, we particularly focus our attention on the TEP data in this

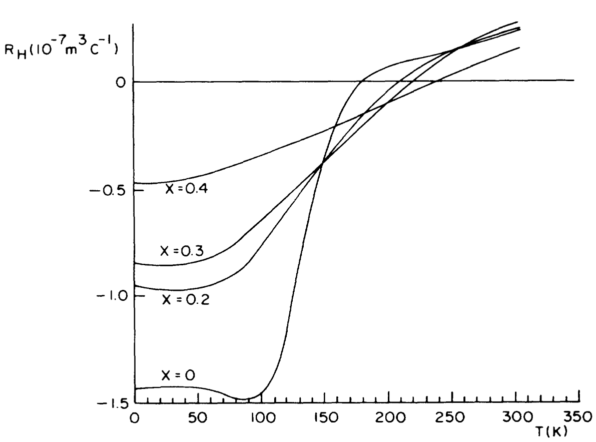

FIG. 2. Temperature dependence of the Hall coefficient R_H for selected $TiSe_{2-x}S_x$ single crystals.

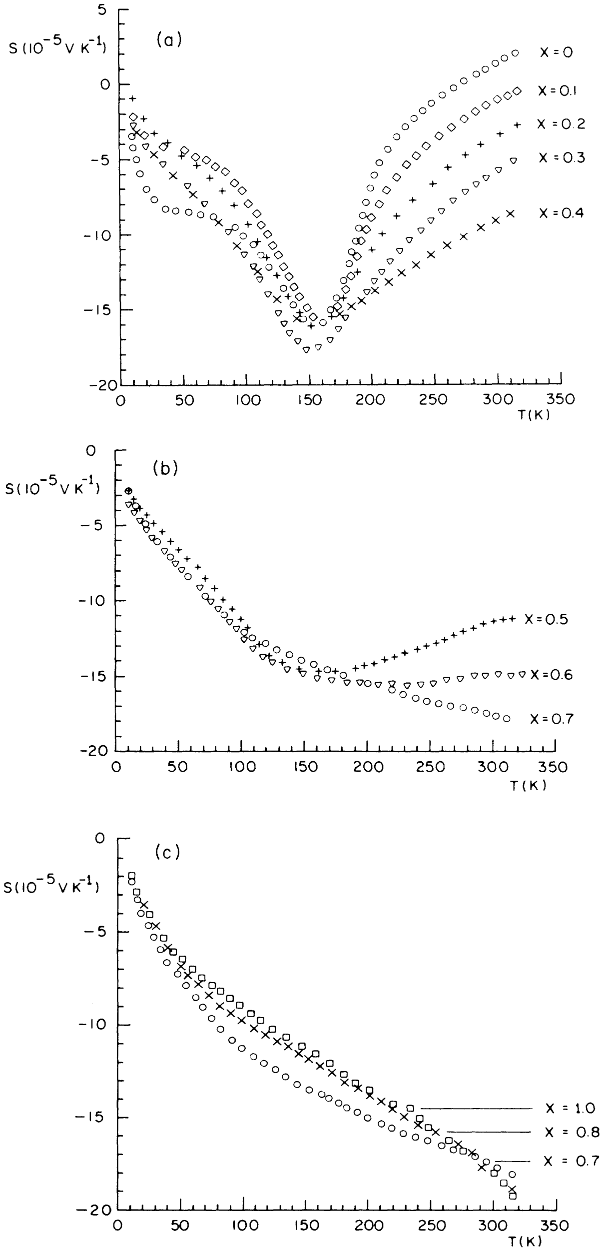

FIG. 3. Thermoelectric power S vs temperature T for transforming [(a) and (b)] and nontransforming (c) $TiSe_{2-x}S_x$ solid solutions. Note that the value $x=0.7$ delimits the boundary between the two cases.

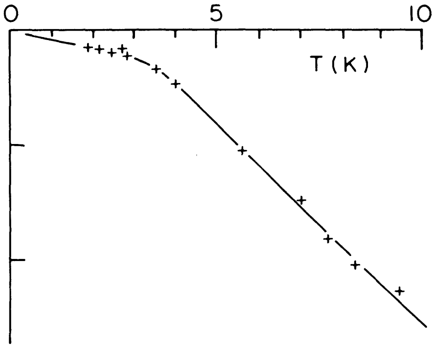

FIG. 4. Low-temperature TEP measurements of $TiSe_2$ down to 1.8 K, showing the linear drift-diffusion regime. The line simply serves as an eye guide.

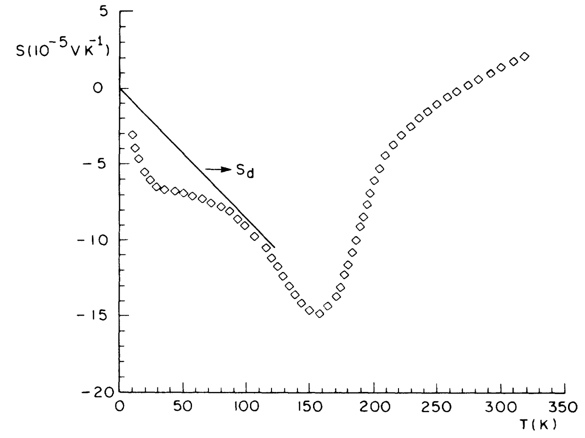

FIG. 5. Linear extrapolation of our low-temperature S_d data, showing its coincidence with the measured TEP around 100 K.

temperature region in order to identify the origin of this plateau. As the linear behavior of the TEP data below 20 K does not extrapolate to zero, we undertook careful measurements down to 1.8 K in $TiSe_2$ using the standard two-flux method.[8] The results, presented in Fig. 4, clearly show how the TEP recovers its 0-K limit with a shoulder around 3.5 K.

III. ANALYSIS AND DISCUSSION

As seen in Fig. 4, the TEP slope increases rapidly with T above 3.5 K. If the TEP were only controlled by drift-diffusion mechanisms, one would expect the opposite behavior. At low temperatures, the electron relaxation time is controlled by impurities (either ionized or neutral) and the TEP slope would be higher (by a factor of 3 or $\frac{3}{2}$, respectively) than that related to the electron-phonon interaction that prevails at higher temperatures. Our results thus confirm that the TEP of $TiSe_2$ at low temperatures is not only controlled by drift-diffusion mechanisms but also by a significant phonon-drag effect which is responsible for the plateau observed below 100 K. Consequently, the total TEP can be written as $S = S_d + S_g$, where S_d and S_g are the drift-diffusion and the phonon-drag contributions, respectively.[9]

To determine S_g, the knowledge of S_d is required. Since S_d of $TiSe_2$ is observed to be linear with temperature below 3 K (see Fig. 4) and expected to remain so until around 100 K (our estimate of the Fermi energy E_F is about 900 K, as shown below), we simply extrapolate linearly our low-temperature data to the plateau high-temperature limit. This is shown in Fig. 5. It is interesting to observe that the measured TEP around 100 K coincides with the extrapolated S_d values, thus identifying the phonon-drag contribution. In order to also obtain an evaluation of S_d for the mixed compounds, we generalize this approach by plotting the tangent to the TEP curve measured around 100 K which passes through the origin. Figure 6 shows the deduced S_g-versus -T values for various x. As can be seen, a minimum of S_g is clearly present around 25 K for small x values. The magnitude of this minimum decreases gradually with increasing x. We also note that S_g is strongly dependent on the sample quality as illustrated by two measured $TiSe_2$ compounds. Nonstoichiometry acts similarly to sulfur addition in reducing the absolute S_g value at a given T. The disappearance of S_g occurs when x approaches 0.7. It is remarkable to note that this value corresponds to the same sulfur concentration that destroys both the phase transition and the large TEP dip around 150 K.

Typically, S_g is given by[9]

$$S_g = S_0 \left[\frac{1/\tau_{e\text{-ph}}}{1/\tau_{e\text{-ph}} + 1/\tau_{\text{ph-ph}} + 1/\tau_{d\text{-ph}}} \right] , \qquad (1)$$

where $S_0 \propto n_e^{-1}$, n_e is the electron concentration, and $\tau_{e\text{-ph}}$, $\tau_{\text{ph-ph}}$, and $\tau_{d\text{-ph}}$ represent the relaxation times of phonons interacting with electrons, other phonons, and defects, respectively. S_g tends to zero at both low and high temperatures and reaches its maximum at an intermediate value of T where the electron-phonon interaction becomes dominant with respect to the other phonon interactions. Our above evaluations of S_g all show this

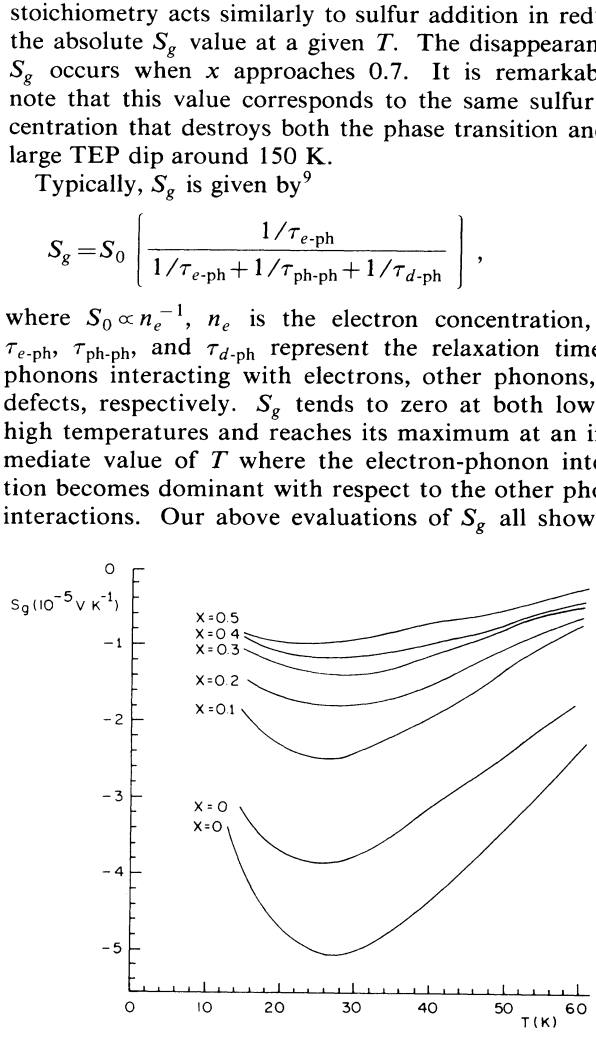

FIG. 6. Plot of S_g versus T for various transforming $TiSe_{2-x}S_x$ compounds, including two $TiSe_2$ samples of different stoichiometry.

behavior qualitatively but the latter becomes less pronounced as x is increased. However, a quantitative treatment of S_g as a function of x is difficult because of the simultaneous dependences of S_0, $\tau_{d\text{-ph}}$, and $\tau_{e\text{-ph}}$ on x. The influence of S_0 is readily seen. This term varies as the inverse of n_e, that is, proportionally to R_H. Indeed, the reduction of S_g is consistent with the observed evolution of R_H when x increases. On the other hand, in the temperature range where S_g is the strongest, $\tau_{d\text{-ph}}$ is mainly limited by mass defects $(\Delta M/M)$.[10] For small x values, $\tau_{d\text{-ph}}$ can be written as[10]

$$\frac{1}{\tau_{d\text{-ph}}(\omega)}=\frac{n_d a^3\omega^4}{4\pi v_s^3}\left[\frac{\Delta M}{M}\right]^2 , \tag{2}$$

where $n_d = x/3$ is the ratio of the number of point defects to the number of lattice sites, $a^3 = V/3$ is the volume occupied by a defect in the lattice, V is the unit-cell volume, v_s is the sound velocity, and ω is the acoustic-phonon frequency. Considering that the substitution of selenium by sulfur introduces negligible variations in the lattice parameters[11] and the sound velocities,[12] $\tau_{d\text{-ph}}$ depends on x only through n_d, so that

$$\frac{1}{\tau_{d\text{-ph}}}=Cx , \tag{3}$$

where C is a constant which can be deduced from Eq. (2). Thus, $1/\tau_{d\text{-ph}}$ acts similarly to S_0 to reduce S_g as x increases. Turning our attention to $\tau_{e\text{-ph}}$, we assume that TiSe$_2$ around 25 K can be described by a single ellipsoidal electronic Fermi pocket,[13] a two-dimensional phonon system,[14] and an intrapocket electron-phonon interaction. Under these conditions, an estimate of $\tau_{e\text{-ph}}$ can be given by[15]

$$\frac{1}{\tau_{e\text{-ph}}}\simeq\frac{2c}{\pi^2}\alpha^2\frac{D^2}{d}\frac{m_\perp^2}{\hbar^3}k_{F\perp}^2 , \tag{4}$$

where c is the interlayer distance, d is the mass density, D is the electron-phonon coupling constant, $m_\perp$ is the in-plane electron effective mass, $k_{F\perp}$ is the transverse Fermi wave number, and $\alpha = k_{F\parallel}/k_{F\perp} = (m_\parallel/m_\perp)^{1/2}$ is the anisotropy ratio. The phonon-drag contribution reaches its maximum value around the temperature[15]

$$T_m=\frac{\hbar\omega_m}{k_B}=\frac{\hbar}{k_B}v_s(2k_{F\perp}) . \tag{5}$$

Since

$$k_{F\perp}=\left[\frac{3\pi^2 n_e}{\alpha}\right]^{1/3} , \tag{6}$$

we see from Eq. (4) that $\tau_{e\text{-ph}}$ varies as $n_e^{-2/3}$ while we expect from Eq. (5) that $T_m \propto n_e^{1/3}$. As n_e increases with x, the influence of $1/\tau_{e\text{-ph}}$ on S_g thus counteracts those of S_0 and $\tau_{d\text{-ph}}$. This could explain why a significant phonon-drag effect is still observed for values of x as large as 0.5 or 0.6. The variation of T_m with x cannot be resolved from our experimental data. This can be due to our evaluation procedure of S_g or, when too many defects are present, to the shortcoming of Eq. (5).

The phonon-phonon relaxation time is not expected to vary strongly with x. Moreover, as $\tau_{e\text{-ph}} \ll \tau_{\text{ph-ph}}$ around 25 K,[16] we ignore the variation of $\tau_{e\text{-ph}}/\tau_{\text{ph-ph}}$ with x in Eq. (1) which can be rewritten for low x values in the following form:

$$\frac{S_0(x)}{S_g(x)}\simeq A + C\tau_{e\text{-ph}}(x)x , \tag{7}$$

where $A = 1 + (\tau_{e\text{-ph}}/\tau_{\text{ph-ph}})$ is close to unity. Considering the proportionality of S_0 with R_H and the dependence of $\tau_{e\text{-ph}}$ on x through n_e and R_H, it is possible to evaluate $C\tau_{e\text{-ph}}(0)$ for TiSe$_2$. For this purpose, we use the experimental R_H and the estimated S_g for the two concentrations $x = 0$ and $x = 0.2$. The result is

$$C\tau_{e\text{-ph}}(0)\simeq 5 . \tag{8}$$

Alternatively, we can deduce the same product $C\tau_{e\text{-ph}}(0)$ from the well-known physical parameters of TiSe$_2$, namely, $c = 6.004\times10^{-10}$ m, $d = 5.2\times10^3$ kg/m^3, $v_s = 2.15\times10^3$ m/s,[17] $m^* = 1.7m_0$ (m_0 is the free-electron mass and $m^* = m_\perp\alpha^{2/3}$ is the density-of-states effective mass) determined from low-temperature specific-heat data,[18] and $n_e = 5\times10^{25}$ m^{-3} as obtained from Hall-coefficient measurements. Then, taking $T_m \simeq 25$ K, Eqs. (5) and (6) yield $k_{F\perp} = 7.6\times10^8$ m^{-1} and $\alpha = 3.3$, and from m^* we get $m_\perp = 0.77m_0$. It is worth noting here that $T_F = (\hbar^2 k_{F\perp}^2/2m_\perp k_B) \simeq 900$ K, which justifies our previous assumption regarding the degeneracy of the electron gas in TiSe$_2$ up to 100 K. It should also be noted that $k_{F\perp}$ and α agree well with the results of band-structure calculations of Suzuki *et al.*[13] for the electron pocket. An estimate of the deformation potential D has been determined by Caillé *et al.*[12] Using our v_s and m^* values in their calculation, we find $D \simeq 0.52$ eV. Equation (4) then gives

$$\frac{1}{\tau_{e\text{-ph}}(0)}\simeq 4.2\times10^8\ \text{s}^{-1} .$$

Evaluating C from Eqs. (2) and (3) for $\omega = \omega_m$, we get $C \simeq 2.4\times10^9$ s^{-1}. Consequently,

$$C\tau_{e\text{-ph}}(0)\simeq 6 , \tag{9}$$

which compares well with Eq. (8). However, considering the various approximations used in the present work, this agreement should be regarded as essentially qualitative.

In conclusion, we unambiguously confirm the characteristics of the 150-K dip in the TEP of all transforming crystals of the TiSe$_{2-x}$S$_x$ family. The evidence of a phonon-drag effect around 25 K, controlled by intrapocket transitions, is established in TiSe$_2$ and related mixed materials with an estimation of the relative magnitude of the electron-phonon and mass defect interactions.

ACKNOWLEDGMENTS

We wish to thank Professor K. Motizuki for providing us with distorted-phase band-structure calculations of TiSe$_2$ prior to publication, and Y. Frongillo for his assiduous technical assistance.

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