Thermoelectric power of TiSe$_{2-x}$S$_x$ mixed crystals at low temperatures

Amir A. Lakhani* and S. Jandl

*Groupe de Recherche sur les Semiconducteurs et les Diélectriques, Département de Physique, Faculté des Sciences,
Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada*

C. Ayache

*Laboratoire de Cryophysique, Service des Basses Températures, Centre d'Etudes Nucléaires de Grenoble,
Boîte Postale 85X, F-38041 Grenoble Cédex, France*

J.-P. Jay-Gerin

*Groupe du Conseil de Recherches Médicales du Canada en Sciences des Radiations,
Département de Médecine Nucléaire et de Radiobiologie, Faculté de Médecine,
Université de Sherbrooke, Sherbrooke, Québec J1H 5N4, Canada
and Département de Physique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Québec J1K 2R1, Canada*

We present thermoelectric power (TEP) measurements, as a function of temperature in the range 7—450 K, of TiSe$_{2-x}$S$_x$ mixed crystals for $x =0$, 0.5, 0.75, 1, and 1.25. A pronounced negative minimum is observed near 150 K in the samples which exhibit the superlattice state. In contrast, in the nontransforming crystals, the TEP varies monotonically with temperature. We interpret the 150-K TEP dip in the transforming samples as due to a phonon-drag effect, in which the strong interaction between electrons and holes and the softening TA-phonon mode L_1^-—the mode actually defining the $2a_0 \times 2c_0$ superlattice condition—plays a primary role.

I. INTRODUCTION

The group-IVB transition-metal dichalcogenide TiSe$_2$, in the 1T layered crystal structure, has received much attention because of its interesting physical properties. It is now well established that stoichiometric defect-free TiSe$_2$ is an intrinsic semimetal due to a small indirect band overlap of about 0.2 eV between the Se-based p-like valence-band maximum at point Γ and the Ti-based d-like conduction-band minimum at point L of the Brillouin zone.[1−16] At room temperature the concentration of holes and electrons is estimated to be about $(2-5) \times 10^{20}$ cm^{-3}.[6,15] The Hall coefficient (R_H) and the thermoelectric power (S), both positive at 300 K, indicate that the p-like holes have a higher mobility than the d-like electrons at this temperature.[2,3,6,9,11,15,17−19] As the temperature is lowered below about 200 K, a second-order structural phase transition develops leading to the formation of a commensurate superlattice phase with new lattice parameters twice as large as those in the high-temperature phase.[20] In contrast to the metallic group-VB transition-metal dichalcogenides, no incommensurate superstructure is found below the transition temperature. Upon formation of the superlattice, both R_H and S convert on cooling to negative sign,[2] indicating that the dominant carrier type passes from p to n between 300 K and lower temperatures. The TiSe$_2$ transition has also the effect of reducing the carrier density from its room-temperature value by a factor of 3−10 at low temperatures.[2,6,21,22] Several mechanisms have been proposed to explain the peculiarities of the 200-K phase transformation in TiSe$_2$. DiSalvo and co-workers[2,6,21] initially suggested, by analogy with the group-VB layered compounds,[23] that the superlattice formation is associated with a charge-density-wave-type instability, where the electron-phonon interaction is strong

enough to produce a distortion when the Γ-point hole and L-point electron Fermi surfaces are near nesting. Wilson and Mahajan proposed[7,20] a pure excitonic insulator (EI) mechanism in which the structural instability arises through a strong Γ-L electron-hole coupling by direct Coulomb interaction. White and Lucovsky argued[24,25] in favor of a soft-phonon-driven antiferroelectric (AF) transition which can be enhanced by the presence of carriers. Finally Hughes[26] proposed a further possible mechanism for the low-temperature transformation, based on a band Jahn-Teller (BJT) effect. Although no general agreement has been established so far among all workers involved to unambiguously identify which mechanism is operative, progress has nevertheless been reported recently. In fact, in an effort to better understand the origin of the superlattice, Friend and co-workers[15,16] performed resistivity and Hall-effect measurements of TiSe$_2$ under pressure and of hydrazine-intercalated TiSe$_2$ between 4.2 and 300 K. Their results showed that the structural phase transition is not critically dependent on the detailed shape and size of the Fermi surface. These authors therefore favored the phonon-driven AF model for the distortion in TiSe$_2$. In a similar effort, Motizuki and co-workers[27−29] developed a microscopic theory of the structural phase transition in TiSe$_2$ on the basis of the BJT mechanism. They calculated phonon dispersion curves by taking into account the effective ion-ion interaction caused by the electron-phonon coupling. They found that the temperature dependence of that effective interaction is able to reproduce the complete softening of the transverse L_1^- phonon mode which corresponds to the observed superlattice structure of TiSe$_2$ below 200 K.[30] These authors thus concluded that electrons and holes plus strong electron-phonon interaction are essential to superlattice formation and softening of the associated zone-boundary phonon. Even if the work of

Friend and co-workers[15,16] and of Motizuki and co-workers[27−29] has undoubtedly reduced the field of investigations on the nature of the phase-transition mechanism, the two emerging pictures, namely, the phonon-instability model and the phonon-mediated electron-hole coupling hypothesis, remain somewhat contradictory. It is the purpose of the present paper to gain additional information related to the origin of the 200-K lattice distortion in TiSe$_2$ sc as to identify which of the proposed mechanisms is most likely operative. Our study is centered on the analysis of the thermoelectric power (TEP) of the mixed system TiSe$_{2-x}$S$_x$ as a function of temperature. As it will become apparent below, TEP measurements are particularly well suited for assessing the relative strength of the phonon-phonon and electron-phonon interactions in this system, and thus for investigating more deeply the nature of the structural transition in TiSe$_2$ and in the transforming TiSe$_{2-x}$ S$_x$ crystals.

The first basal-plane TEP measurements of TiSe$_2$ as a function of temperature were reported by DiSalvo et al.[2] in their study of the electronic properties of this compound in relation with the 200-K superlattice formation. The temperature dependence of the TEP can be described as follows. Between 4 and 40 K it decreases rapidly from a small negative value to about -80 μV K^{-1}. Then it remains nearly constant as the temperature increases from 40 to 90 K. Above about 90 K it decreases again rapidly to a large negative minimum (or dip) of about -150 μV K^{-1} at 150 K. This temperature of 150 K roughly corresponds to the temperature of the observed peak in the electrical resistivity (ρ). From 150 to 300 K, the TEP increases monotonically with temperature, approaching the positive value of about 15 μV K^{-1} at room temperature. DiSalvo et al.[2] mentioned the possibility of a large negative phonon-drag contribution to the TEP of TiSe$_2$ at low temperatures. Recently Gaby et al.[19] have confirmed the low-temperature TEP measurements of DiSalvo et al.[2] on a TiSe$_2$ single-crystal sample slightly less stoichiometric, and have analyzed their data in terms of a dominant phonon-drag effect below about 90 K. In the same study these authors have also measured the TEP of well-characterized Zr$_x$Ti$_{1-x}$Se$_2$ mixed crystals, and have shown that the TEP curves for x =0.03 and 0.11, where the phase transition is still present, exhibit the same general behavior as a function of temperature as that observed for pure TiSe$_2$. However, for the Zr concentration x =0.14, which corresponds to a nontransforming crystal, the TEP curve decreases monotonically with increasing temperature, just like what is observed for stoichiometric TiS$_2$,[31] and the dip at 150 K no longer exists.

The TEP of a conductor at low temperatures can generally be accounted for by the sum of two contributions: $S = S_d + S_{phd}$ where S_d is the drift-diffusion contribution and S_{phd} is the phonon-drag contribution. S_d is due to the normal tendency of the carriers to diffuse through the conductor when a steady temperature difference is maintained across the ends. S_{phd} is produced by the drag of the phonon current on the carriers as a result of the coupling between the phonons and the carriers.[32] In the case of a semimetal such as TiSe$_2$, the analysis of the TEP is complex, two types of carriers being present with their competing contributions both to S_d and S_{phd}. Regarding

the drift-diffusion terms to S, they can be evaluated from other transport data or from ab initio calculations. Then the magnitude of the phonon-drag effects can be assessed once S is measured. Evidently, S_{phd} is very sensitive to the competition between electron-phonon interactions and all other phonon interactions, including the phonon-phonon interaction. Studies of the phonon-drag TEP are thus of particular importance in regard to the determination of the nature of the 200-K phase-transition mechanism in TiSe$_2$. Doping with isoelectronic and isostructural impurities (such as sulfur, zirconium, or hafnium) is also of interest in such studies, for it is known to suppress gradually the phase transformation with increasing impurity concentration while having no drastic effects on the drift-diffusion TEP contribution.

II. EXPERIMENTAL RESULTS

We used iodine-vapor transport to grow homogeneous single-crystal samples of TiSe$_{2-x}$S$_x$. In general, low-growth temperatures (575−650 °C) and excess selenium were used to favor stoichiometry. After growth, chemical analysis showed that deviations from stoichiometry at the growing temperatures used are smaller than the estimated uncertainty in measurements (namely, a few percent). For our TiSe$_2$ samples we found $\rho(165$ K$)/\rho(300$K$) \approx 2.5$.

Typically, the dimensions of our samples were 5 mm long, 1 mm wide, and 0.05 mm thick. Electrical as well as thermal contact was 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° along the sample. At each temperature, plots of thermo emf versus temperature difference as measured by a differential chromel−gold-0.07 at.% Fe thermocouple were made. The TEP was deduced from the gradient of such plots, hence eliminating any contribution from stray emf.
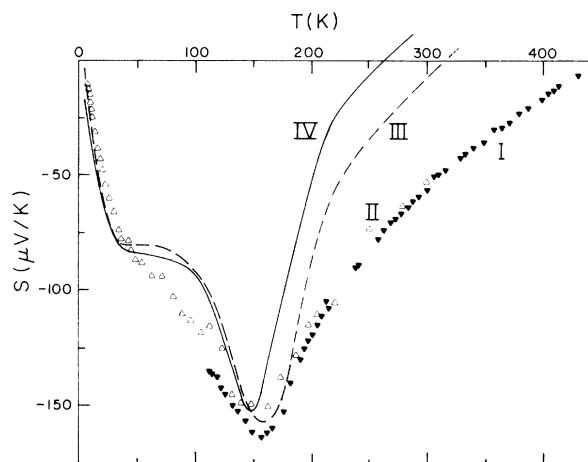
In Fig. 1, TEP measurements of two TiSe$_2$ samples

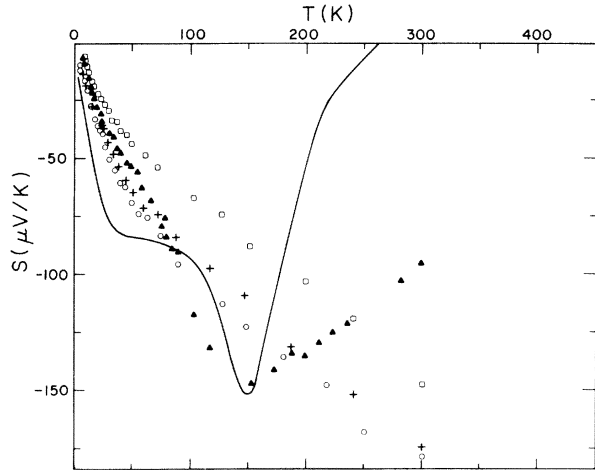FIG. 1. Thermoelectric power S vs temperature T for TiSe$_2$. ▼, △ (curves I and II), this work; — — (curve III), Ref. 19; —— (curve IV), Ref. 2.

FIG. 2. Thermoelectric power S vs temperature T for $TiSe_{2-x}S_x$ with the following sulfur concentrations: $x = 0.5$ (▲), $x = 0.75$ (○), $x = 1$ (+), and $x = 1.25$ (□). The solid curve corresponds to the $TiSe_2$ measurements of Ref. 2.

(curves I and II) are presented along with previous measurements of Gaby et al.[19] (curve III) and of DiSalvo et al.[2] (curve IV). Samples I and II were measured in the temperature ranges (115–450 K) and (7–300 K), respectively. At room temperature the values of S for samples I and II vary noticeably as compared to those for samples III and IV. The magnitude and the position of the dip at 150 K are nearly the same for all samples, while the plateau between 40 and 90 K exists only for samples III and IV. Finally, below 40 K, all samples show the same slope for the variation of S with temperature. The observed differences in $S(T)$ are probably associated with problems of nonstoichiometry.

Figure 2 shows TEP measurements of $TiSe_{2-x}S_x$ single crystals with $x = 0.5$, 0.75, 1, and 1.25 in the temperature range from 7 to 300 K. A dip is observed in $S(T)$ around 150 K for the sulfur concentration $x = 0.5$, while it is completely absent for the other concentrations. The low-temperature S-T slopes of all samples are lower than the corresponding one in pure $TiSe_2$.

III. DISCUSSION

Adding sulfur to $TiSe_2$ is expected to modify many properties of this material. From the normal metal point of view sulfur doping gradually changes its electronic properties from a semimetallic state to a semiconducting state, since it is now established that pure, stoichiometric TiS_2 has no p-d band overlap.[33] Schematically, this can be depicted as a reduction of the dimensions of the Fermi-surface pockets until these latter totally disappear. The phonon spectrum is also expected to change. However, recent studies on similar (semiconducting) layer structures have shown this change to be small for weak doping since only localized modes can be observed.[34] As far as the structural phase transition is concerned, the situation is slightly more complicated. Sulfur doping progressively reduces the transition temperature until the transition itself is completely suppressed for $x > x_c \simeq 0.75$.[2] These results have been confirmed in our $TiSe_{2-x}S_x$ samples by

resistivity (ρ) measurements. We have also verified that the resistivity of our samples shows a temperature dependence in accordance with that obtained by DiSalvo et al.[2] For $x = 0.5$, we observed a shift of the resistivity anomaly towards 100 K. This anomaly was no longer observed for $x > 0.75$. The results of our TEP measurements are discussed below within this context.

The drift-diffusion contribution to the TEP of $TiSe_2$ is apparently dominant both at temperatures below 40 K where the electron carriers are most important, and above room temperature where the role of holes becomes significant. Such an interpretation is consistent with the observed variation of the Hall coefficient as a function of temperature. Upon sulfur doping, Fig. 2 shows that, for $x < x_c$, $S(T)$ is notably affected in both temperature regions as we would expect from a reduction of the band overlap. For $x > x_c$, the larger magnitude of the TEP at room temperature of the nontransforming crystals can be understood on the basis of the extrinsic semiconductor with only electrons contributing to S_d. All the observed changes, however, are much less pronounced than those obtained with a nonsubstitution (such as in the alloy $V_xTi_{1-x}Se_2$).[19] As opposed to these expected drift-diffusion TEP changes, we conclude that the phonon-drag contribution S_{phd} is responsible for the TEP dip around 150 K since the latter is still observable for $x = 0.5$. However, we note that S_{phd} is not significantly modified by the addition of sulfur. This behavior is unlike what is expected in the presence of defects.[35] Instead, the dip seems to be intimately linked with the presence of the structural phase transition, S_d being expected to vary monotonically with temperature just as in TiS_2.[31] The same conclusions also apply to the results of Gaby et al.[19] on the layered crystal alloy $Zr_xTi_{1-x}Se_2$. It is worth noting that, for $x < x_c$, while the position in temperature and the magnitude of the resistivity maximum decrease rapidly with doping,[2] the position and magnitude of the TEP dip remain invariant. The origins for the maximum in $\rho(T)$ and the dip in $S(T)$ are consequently different. This reinforces the interpretation of the TEP dip and of its special features by a phonon-drag effect which is a fundamental characteristic of transforming samples.

The typical efficiency of the electron-phonon coupling in a phonon-drag process is given by

$$\alpha_{\vec{q},\lambda} = \frac{\gamma^{e\text{-ph}}_{\vec{q},\lambda}}{\gamma^{e\text{-ph}}_{\vec{q},\lambda} + \gamma^{ph\text{-ph}}_{\vec{q},\lambda} + \gamma^{i\text{-ph}}_{\vec{q},\lambda}}, \tag{1}$$

where $\vec{q}$ and λ are the phonon wave vector and the polarization index, respectively, $\gamma^{e\text{-ph}}_{\vec{q},\lambda}$ is the absorption coefficient of the phonon $(\vec{q},\lambda)$ due to all possible phonon $(\vec{q},\lambda)$ — electron interactions, and $\gamma^{ph\text{-ph}}_{\vec{q},\lambda}$ and $\gamma^{i\text{-ph}}_{\vec{q},\lambda}$ represent the absorption coefficient of the phonon $(\vec{q},\lambda)$ due to anharmonicity and defects, respectively. S_{phd} can be written in the following form[36]:

$$S_{phd} \propto \sum_{\vec{q},\lambda} f(\omega_{\vec{q},\lambda}) \alpha_{\vec{q},\lambda}, \tag{2}$$

where $f(\omega_{\vec{q},\lambda})$ is the product of the phonon spectral density by the Einstein specific heat for the mode $\omega_{\vec{q},\lambda}$. When $\gamma^{e\text{-ph}} \gg \gamma^{ph\text{-ph}} + \gamma^{i\text{-ph}}$, α approaches unity and the phonon-drag TEP takes its maximum value. Inversely, when $\gamma^{ph\text{-ph}} + \gamma^{i\text{-ph}} \gg \gamma^{e\text{-ph}}$, α is very small resulting in a

negligible phonon-drag effect. As can be seen in Fig. 1 (curves III and IV), a shoulder is observed below about 100 K. Following Gaby et al.,[19] a phonon drag can be invoked. However, this shoulder is attenuated when impurities, nonstoichiometry, or doping are present. In contrast, the dip at 150 K is still present, hardly modified, even in doped samples provided that the phase transition exists. Moreover, the dip occurs in a temperature range where the phonon-phonon interaction is certainly important. A strong electron-phonon absorption is thus needed in order that γ^{e-ph} keep its dominant role in α [see Eq. (1)]. The possibility of such a mechanism is now examined.

A strong electron-phonon interaction near the Kohn[37] condition $\vec{q}=2\vec{k}_F$ (i.e., the phonon wave vector which spans the Fermi surface) has already been invoked by Jay-Gerin and Maynard[38] in order to interpret the dip around 40 K in the TEP of graphite. In this latter material the strength of the interaction results from both the Fermi-surface and the phonon-spectrum anisotropies. The predicted temperature T_K of the TEP dip is given by

$$T_K = \frac{\hbar}{k_B} v_s 2k_F , \qquad (3)$$

where v_s is the velocity of sound, $\hbar$ is the Planck constant divided by 2π, and k_B is the Boltzmann constant. Strictly speaking, such a mechanism is unable to explain the origin of the TEP dip in pure $TiSe_2$ and in the $TiSe_{2-x}S_x$ transforming alloys. Indeed, even if favorable nesting characteristics were preserved with sulfur doping, the shrinking of the dimensions of the Fermi surface would cause a shift in the dip to lower temperatures. This is not observed experimentally, thus confirming the results of Friend and co-workers[15,16] that the phase transformation is not primarily through a change in size and shape of the Fermi surface. It therefore appears that any Fermi-surface nesting configuration is unable to explain our observations. However, in accordance with the prediction of the Kohn effect near a nesting condition, the existence of soft modes in $TiSe_2$ have been established by neutron-diffraction experiments.[30] In particular, this is the case for the TA-phonon mode of wave vector $\vec{\Gamma}L$, labeled L_1^-, which softens significantly with temperature. Evidently, an important phonon absorption should be associated with the energy renormalization of the phonon via Kramers-Kronig—type relations.[39] Such a phonon absorption has recently been observed experimentally in the thermal conductivity of pure $TiSe_2$ which exhibits a pronounced minimum at 150 K.[40] However, neither the existence of the softening phonon mode nor the presence of the phonon absorption are able to decide which of the EI, AF, or BJT mechanisms is operative for the low-temperature superlattice formation in $TiSe_2$. Because of its internal structure [see Eqs. (1) and (2)], S_{phd} allows us to determine this mechanism. Indeed, the EI or AF mechanisms would not necessarily imply an important phonon-drag effect in the TEP. Moreover, the AF mechanism should be correlated with a strong γ^{ph-ph}. This would cause a reduction of the phonon-drag contribution in the transforming crystals, which is contrary to the observation. On the oth-

er hand, the BJT model calls for a strong Γ-L interpocket electron-phonon interaction for the superlattice transition to occur. This model is well correlated with the presence of an important phonon-drag effect in the transforming samples and with its attenuation in the nontransforming ones. The L_1^- phonon, which is known to soften with temperature,[29,30] must play a dominant role in this phonon-drag effect. The TEP dip temperature $T_Q = 150$ K then allows us to evaluate the nonrenormalized energy of this phonon ω_Q to be 110 cm^{-1}, according to the relation

$$k_B T_Q = \hbar \omega_Q . \qquad (4)$$

Since the dip temperature is observed not to vary with sulfur doping, this implies that ω_Q remains unchanged. Actually, theoretical models[30,41] have shown that the phase transition in $TiSe_2$ can be attributed mainly to the instability of the Ti—Se bond length. Since this length is not significantly modified by adding sulfur, the corresponding nonrenormalized energy of the softening phonon remains constant. We also observed that the dip magnitude does not change significantly from sample to sample and with doping in transforming $TiSe_{2-x}S_x$ alloys. This can readily be understood since the general features of the phonon spectrum are not affected appreciably as discussed above. In addition, as long as the electron-phonon interaction is not smeared out by sulfur doping, it not only continues to induce the superlattice phase transformation, but also keeps its leading role in α. Hence the integration in Eq. (2) will not produce any appreciable change in S_{phd}. This is certainly no longer true when the critical nontransforming sulfur concentration is attained.

In conclusion, low-temperature TEP measurements in $TiSe_{2-x}S_x$ alloys and their analysis in terms of a phonon-drag effect illustrate the strong interaction between the electron-hole system and the L_1^- phonon mode and predict the nonrenormalized energy of this latter. The present study clearly favors the BJT model for explaining the origin of the low-temperature lattice distortion in transforming $TiSe_{2-x}S_x$ crystals. However, in order to make the analysis of the TEP more quantitative, the drift-diffusion contributions have to be evaluated precisely. It would also be interesting to complement our experimental studies with Nernst-Ettingshausen measurements, which will enhance the cumulative role of electrons and holes in the phonon-drag effect.

*Present address: The Bendix Advanced Technology Center, 9140 Old Annapolis Rd/Md 108, Columbia, Maryland 21045.

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