### HfTe<sub>5</sub> and ZrTe<sub>5</sub>: Possible polaronic conductors

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The interpretation of the published electrical transport data of the group IVB transition-metal pentatellurides,  $ZrTe_5$  and  $HfTe_5$ , have been reconsidered. These materials evince a strong resistivity peak at a temperature where the Hall effect and the thermopower manifest a change in sign. Inspired by recent investigations of the "metal-insulator transition" in rare-earth manganates, the anomalous behavior of the pentatellurides have been tentatively interpreted as consequences of polaronic transport. [S0163-1829(99)01127-3]

### I. INTRODUCTION—CHARGE-DENSITY WAVES VERSUS POLARONS

The transition-metal pentatellurides HfTe<sub>5</sub> and ZrTe<sub>5</sub> exhibit large, anomalous peaks in the low-temperature resistivity. These peaks occur at approximately 80 and 145 K, respectively, although the exact temperature varies from sample to sample. Similarities in structure between the tellurides and those materials, which exhibit charge-density waves (CDW)-e.g., NbSe<sub>2</sub>-strongly suggested the formation of CDW's as the origin of the resistivity peaks. Around 15 years ago, this suggestion stimulated considerable interest and a flurry of other transport measurements.<sup>1</sup> However, a search for direct evidence of CDW's failed to demonstrate them. Notably absent were superlattice spots in the x-ray diffraction patterns, or evidence of nonlinear electrical conductivity-both hallmarks of CDW formation. In the last 15 years, no other viable suggestions appeared in the literature. The present paper is an attempt to fill the void by exploring another, if tentative, interpretation of the data.

The purpose of the present paper is to investigate the feasibility of using *polaron formation*, instead of CDW formation, as the explanation for the anomalous resistivity peaks. One signature of polaron formation is a peak in the resistivity-vs-temperature curve, which does *not* involve a sudden phase transition. So, it would appear that a mechanism involving polaron transport might explain the observed resistivity anomaly. But can polaron formation also provide an explanation for the many other anomalous properties of HfTe<sub>5</sub> and ZrT<sub>5</sub>?

The theory of one-dimensional charge-density waves, initiated by Peierls and Frohlich,<sup>2</sup> makes clear that a onedimensional metal is inherently unstable against the formation of a charge-density wave. The CDW periodic potential creates an energy gap at the Fermi energy. The lowtemperature state then becomes nonmetallic, provided there are no remaining ungapped bands. If the Fermi surface is segmented, and a band remains ungapped is spite of CDW formation, as is the case for NbSe<sub>2</sub>, a resistivity *maximum* may then result. Quasi-one-dimensional crystals are particularly prone to undergo a Peierls transition.

Theories of polaron formation, on the other hand, owe much to the fundamental papers of Holstein,<sup>3</sup> which discuss the manner with which the electron-phonon interaction

causes self trapping of electrons. Holstein also describes how these self-trapped electrons—called *polarons*—form a conducting band at low temperatures. His theory predicts the existence of a resistivity maximum in the intermediate temperature region between band polarons and self-trapped localized polarons. The "Holstein transition" is a metalinsulator transition with no abrupt onset.

The simplest theory of charge-density waves and the simplest theory of polaron formation each begin with the "Frohlich Hamiltonian," a model with noninteracting electrons coupled to phonons,

$$H = H_{\rm el} + H_{\rm ph} + H_{\rm el-ph}.$$
 (1)

The first term of Eq. (1)  $H_{el}$  represents the kinetic energy of the electrons. The second term  $H_{ph}$  represents the phonon energy, and the third term  $H_{el-ph}$  is the electron-phonon interaction. These energies are conventionally expressed in terms of creation and destruction operators. A onedimensional CDW is achieved when the electron-phonon interaction energy is a small perturbation on the kinetic-energy term  $H_{el-ph} < H_{el}$ . In that case, the ground state of the kineticenergy term is a one-dimensional conduction band, and the electron-phonon term can act to produce a gap at the Fermi energy. The resulting ground state is a CDW—a state that conducts poorly since it is pinned by the inevitable impurities.

On the other hand, a description of a polaronic solid can be achieved when the kinetic energy term is a perturbation on the electron-phonon interaction  $H_{el-ph} > H_{el}$ . In this case, the electron-phonon interaction attracts a cloud of phonons about the otherwise isolated electrons, forming a composite electron-phonon particle, which is called a polaron. At low temperatures, the mutual overlap of these composite particles creates a polaronic band with a heavy mass, but Holstein shows that this band is easily disrupted at elevated temperatures.

There now exist several experimental studies of the pentatellurides displaying anomalous transport properties, the most recent being that of Tritt *et al.*<sup>4</sup> These include measurements of resistivity,<sup>5</sup> thermopower,<sup>6</sup> Hall effect,<sup>7</sup> magnetoresistivity,<sup>8</sup> Shubnikov–de Haas oscillations,<sup>9</sup> and x rays.<sup>10</sup> But no viable theory.

# II. POLARONS

In this paper, we seek to demonstrate that many of the experimental findings concerning tellurides, incompatible with the idea of charge-density waves, have a natural explanation with the assumption that these tellurides are actually poloronic conductors. Throughout this paper, we neglect considerations of the electron-electron interaction.

As we have already mentioned, a polaron is a composite particle composed of an electron and an encircling cloud of lattice displacements. A "polaronic conductor," then, is a solid whose elementary charge carriers are polarons. The polaron's behavior is so strikingly different from that of an electron because the overlap between two polarons is strongly temperature dependent. It is dominated by the overlap between neighboring phonon clouds, which rapidly decreases with increasing temperature. At low temperatures, as a result of purely "elastic" interactions, (those that involve neither creation nor destruction of phonons), the polarons form a band of coherent excitations, which grows progressively narrower as the temperature increases. Coexisting "inelastic" events determine the lifetime of the polaron-band states, thereby increasing the solid's resistivity as the temperature increases. At some intermediate temperature, where the resistivity attains its maximum value, the energy uncertainty is equal to the bandwidth, and the band picture loses its meaning. At higher temperatures, the polaron becomes less and less phase coherent because of the inelastic emission and absorption of phonons. In this regime, the transport is dominated by inelastic hopping processes, and the solid's electrical resistivity is observed to *decrease* with increasing temperature. In this sequence of events-from a metal, (resistivity increases with increasing temperature), to an insulator, (resistivity decreases with increasing temperature)-no sudden phase transition occurs. Rather, a competition between elastic and inelastic events gives rise to a gradual metal-insulator transition. This is the observable feature that first caused us to consider the tellurides as possible poloronic solids.

The study of polarons has recently risen in prominence with the rediscovery of magnetic CMR manganates (where "CMR" stands for "colossal magnetoresistance"), e.g., La2/3Ca1/3MnO3. These materials-mixed rare-earth-alkali earth manganates-are characterized by a metal-insulator transition whose transition temperature is nearly coincident with its magnetic ordering temperature. A very large magnetoresistance is evident in the vicinity of this transition. Such CMR compounds have been shown to be polaronic conductors,<sup>11</sup> and to contain carriers (called composite polarons) composed of electrons surrounded by clouds of both phonons and magnons.<sup>11</sup> Many of these manganates possess abrupt second-order metal-insulator/paramagnetican ferromagnetic phase transition instead of the gradual transition we have hitherto associated with polaronic solids. This sudden phase transition is caused by the magnetic nature of the manganates, where the magnetic exchange interactions can have the effect of precipitating a band collapse. Except for the sudden nature of the transition, the manganates and the tellurides are alike in many respects. Each displays all three poloronic-type regimes: the low-temperature band regime, the mid-temperature metal-insulator regime, and the



FIG. 1. The electrical resistivity ( $\rho$ ), thermoelectric Seebeck coefficient (*S*) and the Hall constant ( $R_{\rm H}$ ) plotted vs absolute temperature for HfTe<sub>5</sub>. All measurements are plotted on an arbitrary vertical scale. The resistivity and thermopower data are taken from Jones *et al.* (Ref. 6), while the Hall-effect data is that of Izumi *et al.* (Ref. 7). The thermopower and Hall constant cross zero near the temperature of the resistivity maximum at approximately 80 K. The coefficients of ZrTe<sub>5</sub> behave in a similar fashion, with the maximum in the resistivity occurring at approximately 145 K.

high-temperature hopping regime. Familiarity with the manganates can help to identify analogous polaronic effects existing in the tellurides. Since tellurides are nonmagnetic, however, the complications of magnons on the poloronic properties of the manganates need to be discounted when considering the pentatellurides. Basically, the pentatellurides are simpler systems.

Recently, Jaime *et al.*,<sup>11,12</sup> in an attempt to substantiate the coexistence of localized and itinerant carriers in the polaronic CMR material  $La_{0.67}Ca_{0.3}MnO_3$ , examined their transport data using the well-known Nordheim-Gorter rule for parallel conducting channels. They utilized a highly intuitive, easily visualized, approximation to the rigorous results of Holstein and his disciples, and we shall also utilize it here to explain the anomalous transport properties of the pentatellurides.

In Fig. 1 the temperature dependence of the resistivity  $\rho(T)$ , thermoelectric coefficient S(T), and Hall-effect coefficient  $R_{\rm H}(T)$  are drawn. At low temperatures, the resistivity of the telluride  $\rho$  is proportional to the square of the temperature, exhibits an anomalous peak at a particular temperature  $T_0$  unaccompanied by any structural anomaly, and then returns to a curve with positive temperature coefficient at even higher temperatures. The Hall coefficient  $R_{\rm H}$  is positive at high temperature (holelike), decreases rapidly near  $T_0$  and becomes negative (electronlike) at the lowest temperatures. The thermoelectric power S is large and positive at high temperatures (holelike) drops precipitously and crosses zero near  $T_0$ , reaches a large negative peak (electronlike), and decreases to zero at the lowest temperatures in a metallic fashion. Any viable theory should, at a minimum, explain these fundamental transport results.

## **III. RESISTIVITY**

Following the example of Jaime *et al.*,<sup>12</sup> we express the resistivity as a parallel combination of coexisting localized and itinerant carriers. (This concept has its first-principles



FIG. 2. Temperature dependence of the normalized resistance [R(T)/R(300)] along the *a* axis of ZrTe<sub>5</sub>. Filled circles are data points from Okada *et al.* (Ref. 10). Solid line is a fit to polaron theory, [Eq. (2)], using the parameters found within the text.

justification in Holstein's<sup>3</sup> classic papers on polaron transport. See his Fig. 1, p. 369, and the accompanying discussions, or in subsequent reviews by other authors.)

$$\rho(T) = [f(T)/\rho_{\rm lt}(T) + \{1 - f(T)\}/\rho_{\rm ht}(T)]^{-1}, \qquad (2)$$

where  $\rho_{lt}$  is the low-temperature itinerant-carrier resistivity,  $\rho_{ht}$  is the high-temperature localized-carrier resistivity, and f(T) is the fraction of the carriers that are in the metallic state. We choose

$$\rho_{\rm ht} = AT \exp(E_{\rm pol}/kT), \qquad (3a)$$

$$\rho_{\rm lt} = BT^2, \tag{3b}$$

$$f(T) = (1/2) \{ 1 - \tanh[(T - T_0)/\Delta) ] \}, \qquad (3c)$$

where Eq. (3a) (with the temperature-dependent prefactor) is the form expected for the adiabatic hopping of small polaron.  $E_{pol}$  is the polaron-activation energy, and f(T) is a reasonable function that fits the two halves of the resistivity curve together. A, B,  $\Delta$ ,  $E_{pol}$ , and  $T_0$  are constants that are to be determined by the data, and have an obvious physical significance for each particular sample. (The crossover temperature  $T_0$  has been estimated by Holstein<sup>3</sup> as half the Deby temperature.)

In Fig. 2, we reproduce the *a* axis normalized resistance R(T)/R(300 K) of ZrTe<sub>5</sub>. The filled circles are data points from Okada *et al.*,<sup>10</sup> while the solid line is a fit the phenomenological polaron theory, Eqs. (2) and (3). The theoretical fit is able to reproduce many of the features characterizing the data, including the resistivity peak near 150 K and the resistance upturn at high temperatures. (However, the latter feature can also be due to a small leftover piece of the Fermi surface, which does not undergo polaron formation but not included in the theory.) The parameters characterizing the fit of Eq. (3) to the ZrTe<sub>5</sub> resistance data are (in obvious units, which are in agreement with Fig. 2):  $T_0=184 \text{ K}$ ,  $\Delta=33 \text{ K}$ ,  $\rho_0=0.34$ ,  $B=1.7\times10^{-4}$ , and  $E_{\text{pol}}/k=204.5 \text{ K}$ .

The electrical resistance [with each composition normalized to R(300 K)] of  $Zr_{1-x}Hf_xTe_5$ , as measured by DiSalvo *et al.*,<sup>1</sup> is shown for different compositions from 4.2 to 300 K in Fig. 3. A smooth progression from pure Zr to pure Hf is evident, with higher peak temperature associated with lower values of the resistivity maximum. This behavior is not ob-



FIG. 3. The electrical resistance (each curve normalized to R[300 K]) of  $Zr_{1-x}Hf_xTe_5$ , (dashed lines), published by DiSalvo *et al.* (Ref. 1). The solid line is a fit of the expression  $\rho_{MAX} \propto T \exp(E_{pol}/T)$  to the resistivity peaks.

served in related CDW materials such as NbSe<sub>3</sub> or TiSe<sub>2</sub>. In CDW materials the resistive anomaly is rapidly removed by alloying, since cation disorder rapidly suppresses the phase transition. On the other hand, the polaronic rare-earth manganates containing various rare-earth substitutions<sup>13</sup>—for example (La<sub>1-x</sub>Gd<sub>x</sub>)<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub> or (La<sub>1-x</sub>Pr<sub>x</sub>)<sub>0.67</sub>Ca<sub>0.33</sub>MnO<sub>3</sub>)—display very similar behavior to that shown in Fig. 3. Poloronic considerations for these manganates led Dionne<sup>13</sup> to a relationship between the magnitude of the resistivity peak  $\rho_{MAX}$  and the peak temperature  $T_0$ .

$$\rho_{\rm MAX} \propto T_0 \exp(E_{\rm pol}/kT_0), \qquad (4)$$

where  $E_{pol}$  is the polaron-activation energy, and the temperature-dependent prefactor is a characteristic of the polaron. The solid line in Fig. 3 is a fit of Eq. (4) to the resistivity peaks of  $Zr_{1-x}Hf_xTe_5$ . (This curve, of course, wrongly assumes that the number of carriers and the polaronic activation energy are independent of *x*. It remains, however, a good approximation.)

#### **IV. HALL EFFECT**

Two facts are evident upon inspection of the temperature dependence of the Hall effect (Fig. 1): (a) The Hall constant, initially positive, changes sign as the temperature increases. (b) At high temperatures, the Hall constant decays in an exponential fashion, with an activation energy close in magnitude to the activation energy, which characterizes the resistivity. These two phenomena can be discussed within the context of polaron theory.

It is not the purpose of this paper to explain how the seemingly innocent Lorentz force leads to subtle problems involving quantum phases when quantum mechanics is applied to the treatment of the Hall effect. Brief outlines of polaronic Hall-effect theory can be found in the concise reviews of Friedman and Emin.<sup>14</sup> As one might expect. quantum treatment of the Hall coefficient  $R_H$  yields answers not far from to the classical, effective-mass-independent result when applied to band-polarons at low temperatures

$$R_{\rm H}(T \to 0) \sim (ne)^{-1}, \tag{5}$$



FIG. 4. Temperature dependence of the HfTe<sub>5</sub> Hall constant. Filled circles are data points from Izumi *et al.* (Ref. 7). Solid line is a fit to polaron theory, [Eq. (6)], using the parameters stated in the text. The Hall coefficient is small at room temperature, gradually increases to a positive peak at about 90 K, then decreases abruptly and passes through zero at 76 K. It remains negative at low temperatures.

where n is the density and e is the charge of the carriers, including its algebraic sign (negative for electrons, positive for holes), and the equation is expressed in SI units. Thus, at low temperatures, a negative sign (the case for the tellurides) is associated with electrons. The HfTe<sub>5</sub> Hall coefficient exhibits a sign reversal near the temperature of maximum resistivity. At higher temperatures, in the hopping regime, both Hf and Zr pentatelluride Hall constants have a positive sign, and their magnitudes decrease to zero as the temperature further increases. The positive sign of the Hall constant is conventionally associated with holes, and a sign reversal usually indicates the existence of multiple Fermi surfaces in most materials. However, small polaron theory reveals, surprisingly, that a sign reversal in the Hall coefficient can result from purely electronlike carriers in the localized regime if: (a) hopping between nearest neighbors only need be considered, (b) this hopping is between antibonding orbitals (those on the bonds), and (c) the smallest closed-loop network of atoms in the crystal contains an odd number of bonds (e.g., three). The pentatelluride structure contains onedimensional chains of end-sharing ZrTe<sub>6</sub> (HfTe<sub>6</sub>) trigonal prisms,<sup>5,15</sup> providing the necessary odd-membered rings necessary for the anomalously signed Hall effect. Two bandstructure calculations have been published,<sup>15</sup> at odds with each other in some essential details, but agreeing that the pentatellurides are semimetals (with nearly filled, slightly overlapping bands at the Fermi surface) and that at least one of the two overlapping bands originates primarily from the tellurium p orbitals. Thus, at present, neither band structure explicitly conflicts with a polaronic interpretation of the sign anomaly. A high-temperature upturn in the resistivitytemperature curve suggests that there may exist a nonpolaronic band in addition to the polaronic band herein discussed; but the polaron formula per se [Eq. (6), below] can also predict an upturn without the explicit introduction of another band.

In Fig. 4, we reproduce the temperature dependence of the HfTe<sub>5</sub> Hall coefficient. The filled circles are data points from Izumi *et al.*<sup>7</sup> The solid line is a fit to a phenomenological polaron theory, Eq. (6), below. The Hall constant is large

(for a metal) and positive at room temperature, and increases with decreasing temperature. It has a peak at about 90 K, then decreases abruptly with decreasing temperature and passes through zero at 76 K, where the resistivity curve peaks. Thereafter,  $R_{\rm H}$  remains negative at low temperatures. The relatively large magnitude of  $R_{\rm H}$  at low temperatures indicates the presence of a small electronlike band of electrons (polarons), containing only a fraction of an electron per atomic site, which disrupt into self-trapped polarons at higher temperatures. The most notable feature of this curve is the sign reversal.

Just as with the resistivity, we consider the temperature dependence of the Hall voltage to arise from the coexistence of polaronic and band-electron fractions conducting in parallel. The low-temperature band-electron Hall coefficient has a nearly temperature-independent value with a magnitude of order  $\sim (ne)^{-1}$ . The high-temperature polaronic Hall constant decays with increasing temperature, characterized by an activation energy,  $E_{\rm H}$ , which is smaller than the activation energy  $E_{\rm pol}$ . In the case of the tellurides, the high- and low-temperature contributions to the Hall constant are of opposite sign. The temperature-dependent polaronic Hall constant is expressed as

$$R_{\rm H}(T) = [f(T)][-A] + [1 - f(T)][B \exp(-E_{\rm H}/kT)],$$
(6)

where A, B, and  $E_{\rm H}$  are constants to be determined by the fitting procedure. As before, f(T) represents (in an approximate manner) the temperature dependence of the fractional polaron-band electrons. The parameters characterizing the fit of Eq. (6) to the HfTe<sub>5</sub> Hall-effect data are (in units which are in accord with the units used in Fig. 4):  $T_0 = 77.3$  K,  $\Delta = 7.6$  K,  $A \sim (ne)^{-1} = 1.55$ , B = 36, and  $E_H/k = 30$  K.

### **V. THERMOPOWER**

The Seebeck thermopower coefficient S like the Hall constant  $R_H$  is negative at low temperature, and changes sign at a temperature near the resistivity-maximum point. Thermodynamic considerations demand that S=0 at absolute zero. (In these considerations, we will assume that S is entirely electronic in origin, and we will ignore the effect of phonon drag.) At high temperatures S(T) is positive, and decreases with increasing temperature at a rate much slower than  $\rho(T)$ or  $R_{\rm H}(T)$ , as indicated in Fig. 1. The large room-temperature thermopower recently prompted Tritt and coworkers to repentatellurides evaluate the for thermoelectric applications.<sup>4,16</sup> A characteristic of polaron motion is a difference between the activation energy for conduction  $E_{\alpha}$  and that for thermopower  $E_s$ . [In the high-temperature polaronic hopping regime,<sup>11</sup> the Seebeck coefficient is represented by the formula,  $S = (k/e) \{E_s/kT + \text{const.}\}$ .] A signature of polaron formation is the smaller "activation energy" deduced from thermopower compared to the activation energy deduced from polaron hopping  $E_{\rm S} < E_{\sigma}$ . Indeed, it is possible for polaron thermopower to become temperature independent at high-enough temperatures. The high-temperature thermopower of HfTe<sub>5</sub> (Figs. 1 and 5) is clearly less temperature dependent (has a smaller activation energy) than the resistivity, which is taken as an indication of polaron formation in this material. (Perhaps, we can attribute the slight



FIG. 5. Temperature dependence of the thermoelectric  $ZrTe_5$ Seebeck coefficient, taken from Jones *et al.* (Ref. 6). Solid line is a fit to polaron theory, [Eq. (8)], using the parameters stated within the text.

upturn of the thermopower above 250 K to the existence of an additional nonpolaronic band, segmented from the polarons.)

The thermopower is a measurement of the entropy per carrier. At low temperatures, the thermoelectric power reaches a large negative peak and decreases to zero in a metallic fashion. The sign of the low-temperature Seebeck coefficient is in agreement with the sign of the low-temperature Hall effect, indicating that the low-temperature band polarons are primarily assembled out of *n*-type electrons. At high temperatures, in the hopping regime, the thermopower attains a constant value (when all the polarons are released from their trapping sites by the high temperature, which we loosely term the "infinite" temperature), given by the modified Heikes equation<sup>17</sup>

$$S(\infty) = -(k/|e|)\ln[(1-c)/c] - (k/|e|)\ln 2, \quad (7a)$$

where the first term is the contribution of the configurational entropy and the second is the contribution of the spin entropy to the thermopower. Here, *c* is the ratio of the number of carriers to the number of sites, and (k/e) is a numerical constant equal to 86  $\mu$ V/K,—a characteristic value for Seebeck coefficients.  $S(\infty)$  possesses a positive sign only when c > 0.67. Using the experimental value,  $S(\infty) =$  $+ 69 \mu$ V/K, for HfTe<sub>5</sub> obtained from Fig. 5, the sign and value of the high-temperature thermoelectric power, deduced from Eq. (7a), indicates the HfTe<sub>5</sub> polaron ''band'' to be about half full, ( $c \sim 0.5$ ), seemingly in strong disagreement with its low-temperature electronlike properties and with the small concentration of polarons deduced from the Hall effect.

The observed positive sign of the Seebeck coefficient seems, at first sight, to conflict with the polaron interpretation, an interpretation that predicts a negative value when the polaron concentration is small. However, if we interpret c, [the concentration of polarons in Eq. (7a)], as the "effective" concentration (i.e., the number of polarons per *available* site)—and if the number of sites available to the polaron

is small—it is possible to obtain a *positive* Seebeck coefficient from Eq. (7a). Such reinterpretations are not uncommon in the literature, and we shall proceed as if the observed sign of the thermopower was consistent with a polaronic interpretation.

At low temperatures, in the polaronic-band regime, the sign of the Seebeck coefficient is that of the negative charge carriers, with the magnitude decreasing to zero with decreasing temperature.

$$S(T \to 0) = -(k/|e|)(T/T_{\rm F}).$$
 (7b)

In the above expression,  $T_{\rm F}$  is a characteristic temperature of the same order of magnitude as the Fermi temperature, and the negative sign is a characteristic of the charge carrier.

In Fig. 5, we display the temperature dependence of the thermoelectric  $ZrTe_5$  Seebeck coefficient, taken from the work of Jones *et al.*<sup>6</sup> The filled circles are data points and the solid line is a fit to a phenomenological polaron theory of the Seebeck coefficient,

$$S(T) = [f(T)][-cT] + [1 - f(T)][S(\infty)], \qquad (8)$$

where c and  $S(\infty)$  are constants to be determined by the fitting procedure and f(T) is given by Eq. (3c). In this equation, we have intentionally omitted the "thermopower activation energy" term— $(k/e)(E_S/kT)$ —in order to further simplify the expression. The parameters characterizing the fit of Eq. (5) to the ZrTe<sub>5</sub> Seebeck coefficient data of Fig. 5 are (in units compatible with the units of Fig. 5):  $T_0 = 142$  K,  $\Delta = 21$  K, c = 0.55,  $S(\infty) = 69$ .

### **VI. CONCLUSION**

A decade of inactivity has elapsed since the discovery of the many anomalies in the transport properties of hafnium and zirconium pentatelluride. During this period, no explanation of these phenomena has been offered. Recently, Tritt and coworkers have revived interest in these compounds by suggesting a possible practical application of these compounds—thermoelectric heat exchangers. The preceding sections of the present publication rely on the theory of polaron formation to offer an explanation of these phenomena. By utilizing a phenomenological methodology, previously utilized for CMR materials, certain fundamental chargetransport properties of the pentatellurides have acquired a very reasonable explanation.

At low temperatures, polarons jump elastically from site to site by way of quantum-mechanical transitions, while at high temperatures, polarons hop via a thermal excitation process involving an activation energy. The resistivitymaximum observed in HfTe<sub>5</sub> and ZrTe<sub>5</sub> is explained as a thermal crossover between these two processes. The temperature-dependence of the Hall effect and the thermopower, including their anomalous signs, are explained in a similar fashion, although the "infinite temperature" thermoelectric coefficient may not be well explained here.

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- <sup>1</sup>F. J. DiSalvo, R. M. Fleming, and J. V. Wazczak, Phys. Rev. B 24, 2935 (1981); C. M. Jackson, A. Zettl, G. Gruner, and F. J. DiSalvo, Solid State Commun. 45, 257 (1983); M. Izumi, K. Uchinokura, S. Harada, R. Yoshizaki, and E. Matsuura, Mol. Cryst. Liq. Cryst. 81, 141 (1982); E. J. Skelton, T. J. Wieting, S. A. Wolf, W. W. Fuller, D. U. Gubser, T. L. Francavilla, and F. Levy, Solid State Commun. 42, 1 (1982).
- <sup>2</sup>R. E. Peierls, *Quantum Theory of Solids* (Oxford University Press, Oxford, 1955), p. 108; H. Frolich, Proc. R. Soc. London, Ser. A **223**, 296 (1954).
- <sup>3</sup>T. Holstein, Ann. Phys. 8, 325 (1959); 8, 343 (1959).
- <sup>4</sup>T. M. Tritt, M. I. Wilson, R. L. Littleton, Jr., C. Feger, J. Kolis, A. Johnson, D. T. Verebelyi, S. J. Hwu, M. Fakhruddin, and F. Levy, in *Thermoelectric Materials—New Directions and Approaches*, edited by T. M. Tritt *et al.*, MRS Symposia Proceedings No. 478 (Materials Research Society, Pittsburgh, 1997), p. 249.
- <sup>5</sup>S. Okada, T. Sambongi, and M. Ido, J. Phys. Soc. Jpn. **49**, 839 (1980); M. Izumi, K. Uchinokura, and E. Matsuura, Solid State Commun. **37**, 641 (1981); F. J. DiSalvo, R. M. Fleming, and J. V. Waszczak, Phys. Rev. B **24**, 2935 (1981).
- <sup>6</sup>W. W. Fuller, S. A. Wolf, T. J. Weiting, R. C. LaCoe, P. M. Chaikin, and C. Y. Huang, J. Phys. C **44**, c3-1709 (1983); T. E. Jones, W. W. Fuller, T. J. Wieting, and F. Levy, Solid State Commun **42**, 793 (1982).
- <sup>7</sup>M. Izumi, K. Uchinokura, E. Matsuura, and S. Harada, Solid State Commun. **42**, 773 (1982).
- <sup>8</sup>R. T. Littleton, M. L. Wilson, C. R. Feger, M. T. Marone, J. Kolis, and T. M. Tritt (unpublished); M. Izumi, K. Uchinokura, E. Matsuura, and S. Harada, Solid State Commun. **42**, 773 (1982).
- <sup>9</sup>G. N. Kamm, D. J. Gillespie, A. C. Ehrlich, T. J. Wieting, and F.

Levy, Phys. Rev. B **31**, 7617 (1985); M. Izumi, K. Uchinokura, R. Yoshizaki, S. Harada, T. Nakayama, A. Yamada, and E. Matsuura, J. Phys. C **44**, C3-1705 (1983); G. N. Kamm, D. J. Gillespie, A. C. Ehrlich, D. L. Peebles, and F. Levy, Phys. Rev. B **35**, 1223 (1987).

- <sup>10</sup>S. Okada, T. Sambongi, M. Ido, Y. Tazuke, R. Aoki, and O. Fujita, J. Phys. Soc. Jpn. **51**, 460 (1982); F. J. DiSalvo, R. M. Fleming, and J. V. Waszczak, Phys. Rev. B **24**, 2935 (1981).
- <sup>11</sup>M. Jaime, M. B. Salamon, M. Rubinstein, R. E. Treece, J. S. Horwitz, and D. B. Chrisey, Phys. Rev. B 54, 11 914 (1996); A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. 74, 3407 (1995); J. Zang, A. R. Bishop, and H. Roder, Phys. Rev. B 5, R8840 (1996); L-J. Zou, H. Q. Lin, and Q-Q. Zheng, J. Appl. Phys. 83, 7363 (1998).
- <sup>12</sup>M. B. Salamon, Bull. Am. Phys. Soc. 44, 337 (1999).
- <sup>13</sup>G. F. Dionne, J. Appl. Phys. **79**, 5172 (1996); M. Rubinstein, D. Gillespie, J. E. Snyder, and T. Tritt, Phys. Rev. B **56**, 5412 (1997); H. Y. Hwang, S.-W. Sheong, P. G. Radaelli, M. Marezio, and B. Batlogg, Phys. Rev. Lett. **75**, 914 (1995).
- <sup>14</sup>L. Friedman, Philos. Mag. **38**, 467 (1978); D. Emin, in *Science and Technology of Magnetic Oxides*, edited by M. R. Hundley, J. H. Nickel, R. Ramesh, and Y. Tokura, MRS Symposia Proceedings No. 494 (Materials Research Society, Pittsburgh, 1998), p. 163.
- <sup>15</sup>D. W. Bullett, Solid State Commun. **42**, 691 (1982); M. H. Whangbo, F. J. DiSalvo, and R. M. Fleming, Phys. Rev. B **26**, 687 (1982).
- <sup>16</sup>R. T. Littleton IV, Terry M. Tritt, C. R. Fegelr, J. Kolis, M. L. Wilson, and M. Marone, Appl. Phys. Lett. **72**, 2056 (1998).
- <sup>17</sup>C. Wood, Rep. Prog. Phys. **57**, 459 (1988); P. M. Chaiken, in *Organic Superconductivity*, edited by V. Z. Kresin and W. A. Little (Plenum, New York, 1990), p. 101; P. M. Chaikin and G. Beni, Phys. Rev. B **13**, 647 (1976).