



Unusual Transport and Strongly Anisotropic Thermopower in PtCoO₂ and PdCoO₂

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We show, using Boltzmann transport calculations and analysis of experimental data, that hexagonal PdCoO₂ and PtCoO₂ have a highly unusual metallic transport. The in-plane transport is typical of a very good metal, with high conductivity and low positive thermopower. The *c*-axis transport is completely different, with 2 orders of magnitude lower, but still coherent, conductivity and remarkably a very large negative thermopower. This large anisotropy of the thermopower provides an opportunity for investigating transport in a highly unusual regime using bulk materials.

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Electronic transport in metals is a well studied area of physics. Nonetheless, there remain ongoing puzzles such as the behavior of different materials at and beyond the Ioffe-Regel limit (The point where Boltzmann theory breaks down, i.e. $l = a$, where l is the mean free path needed to explain the resistivity and a is the lattice spacing). Dimensionality plays a crucial role in the theory of metallic transport. For example, two-dimensional metals behave in a qualitatively different way with respect to disorder induced localization than three-dimensional materials [1]. Experiment has played an important role in defining challenges to our understanding of transport. For example, the nonsaturation of the resistivity of certain materials at the Ioffe-Regel limit has attracted much theoretical interest, motivated in part by the remarkable physical properties that some of these materials such as cuprates and doped fullerenes display [2,3]. In general, these materials are in a regime where electron-phonon and scattering from other bosons (e.g., spin fluctuations) are important as opposed to low T , where point defect, boundary, and electron-electron scattering usually dominate. One difficulty is a lack of good model systems spanning the range of extremely anisotropic behavior in transport and showing T -dependent dimensional crossover at ordinary temperatures. Materials that show extreme behavior at the Boltzmann level and can be grown as high-quality crystals can define the limits to conventional transport behavior and perhaps lead to discovery of novel phenomena. The thermopower $S(T)$ provides a particularly useful probe because it is very sensitive to localization and because it can be calculated from band structures at the Boltzmann level by making the constant scattering time approximation, which is typically valid for metals. This allows direct comparison between expectations at the Boltzmann level and experiments.

Here we show by a combination of Boltzmann transport calculations and analysis of experimental data that the hexagonal delafossite structure oxides PdCoO₂ and PtCoO₂ are in a particularly interesting regime. These materials show excellent metallic properties in-plane, but

are much poorer metals in the *c*-axis direction. PdCoO₂ is coherent in both directions, while it is estimated that PtCoO₂ is close to the Ioffe-Regel limit along *c* at room temperature. This is unlike other highly anisotropic materials, such as cuprates, which have incoherent transport in the out-of-plane direction at room temperature. The conductivity anisotropies within the constant scattering time approximation are temperature dependent, but are still well in excess of 100 even above room temperature consistent with experimental data. The *c*-axis transport behaves as a very heavy band metal in resistivity and an intrinsic semiconductor in thermopower, $S \sim -200 - 300 \mu\text{V/K}$. The in-plane $S(T)$ is much smaller characteristic of a normal good metal and has opposite (positive) sign. The anisotropy of $S(T)$ is very unusual and places these compounds in a unique transport regime.

Importantly, both materials can be grown as good single crystals [4,5]. PdCoO₂ has been more extensively studied than PtCoO₂. Tanaka and co-workers [6] reported an in-plane resistivity $\rho(260 \text{ K}) \sim 4.7 \mu\Omega \text{ cm}$, which is exceptionally low for an oxide, and $\rho(260 \text{ K})/\rho(16 \text{ K}) \sim 8$. Recently, Takatsu and co-workers reported crystals with in-plane $\rho(300 \text{ K})/\rho(1.6 \text{ K}) \sim 400$ and were able to observe quantum oscillations. First principles calculations show a simple Fermi surface consisting of a corrugated cylinder derived from Pd *s* and *d* states. [7–10] PtCoO₂ is less studied. However, its electronic structure has been investigated by resonant photoemission [11], and density functional calculations [7,8]. Both compounds show Pauli paramagnetic behavior at low temperature with no magnetic transitions [5,6,12]. The very high in-plane conductivities and the fact that the conductivities are strongly anisotropic were explained in terms of the Pd/Pt dominated electronic structure near the Fermi energy (E_F) based both on first principles calculations and experiments including angle resolved photoemission (ARPES) and other spectroscopies [7–11,13,14].

Our transport calculations were performed using the standard Boltzmann theory for metals [15] based on the density functional electronic structure as obtained with the

generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) [16]. We used the general potential linearized augmented plane wave (LAPW) method [17], as implemented in the WIEN2K package [18]. The needed Fermi surface integrals were obtained with the BOLTZTRAP code [19]. The computational parameters are similar to our prior study of the electronic structure of PdCoO₂ [10], except that we used a much more dense Brillouin zone sampling for transport calculations and in the case of the 5*d* compound PtCoO₂ included spin-orbit. We tested different augmentations (standard LAPW and augmented plane wave plus local orbital [20]), different choices of sphere radii and other convergence parameters. The calculations are based on the experimental lattice parameters, *a* and *c* [6], but we relaxed the internal O coordinate. The values are *z*_O = 0.1125 for PdCoO₂ and *z*_O = 0.1122 for PtCoO₂ in accord with experiment and prior calculations [7,8,10].

Our electronic structure for PdCoO₂ is given in Ref. [10]. The band structure of PtCoO₂ is shown in Fig. 1. The Fermi surface (Fig. 2) is a single large electron cylinder centered around the Γ -Z line and with a hexagonal shape that is rotated 30° with respect to the zone, similar to the Pd compound. This nearly 2D surface shows apparent nesting between the flat, concave faces of the hexagons. Nonetheless, no charge density or spin density wave instabilities are seen experimentally. This is presumably a consequence of the high band velocity (see below). The corners of the Fermi surface are along the Γ -F direction. This is similar to PdCoO₂. In both compounds the Fermi surface contains one electron (1/2 the zone). Within the Boltzmann theory the transport parameters at low *T* can be expressed as integrals over the Fermi surface of band structure quantities and scattering rates, while at finite *T*, the formulas are the same, but involve integrals with Fermi distributions. These simplify greatly if one makes the constant scattering time approximation. Within this approximation, the scattering rate $\tau(\mathbf{k}, E)$ is assumed to be independent of momentum and energy. This does not, however, involve any assumption about doping level or *T* dependence. With this approximation, τ cancels in $S(T)$, which can then be calculated directly from the band structure [19].

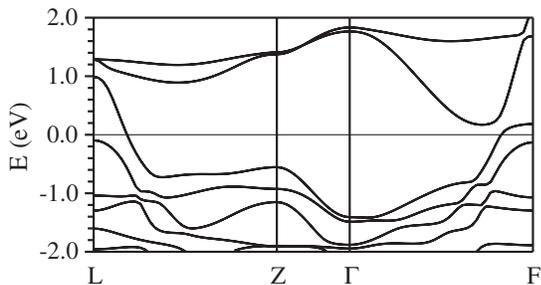


FIG. 1. Calculated band structure of PtCoO₂ around E_F , which is at 0 eV, including spin orbit.

As mentioned, we find very large conductivity anisotropies. The calculated value is 260 K is $\sigma_{xx}/\sigma_{zz} = 120$ for PdCoO₂. This compares reasonably with the measured value of 150 at this temperature [6]. For PtCoO₂ we obtain a ratio of ~ 500 at 260 K. However, there is a large uncertainty due to the small conductivity out-of-plane, which is in the denominator. The calculated values decrease with *T* due mainly to an increase in σ_{zz}/τ (see [10]). The effective transport Fermi velocities at 260 K (from Fermi surface integration with a 260 K broadening) are $\langle v_x^2 \rangle^{1/2} = 3.9 \times 10^5$ m/s and $\langle v_z^2 \rangle^{1/2} = 3.5 \times 10^4$ m/s for PdCoO₂. The values for PtCoO₂ are $\langle v_x^2 \rangle^{1/2} = 5.6 \times 10^5$ m/s and $\langle v_z^2 \rangle^{1/2} = 2.4 \times 10^4$ m/s. Noh and co-workers [13] measured the band dispersion of PdCoO₂ along the 2D Γ -*M* direction using ARPES. This direction intersects the faces of the hexagon shaped Fermi surface, which is a high velocity direction. Their band velocity of 4.96 eV/Å agrees well with our value of 4.72 eV/Å for this direction. One may use the measured $\rho_{xx}(260 \text{ K}) = 4.689 \mu\Omega \text{ cm}$ for PdCoO₂ with these velocities to get an inverse scattering rate, $\tau(260 \text{ K}) = 5.8 \times 10^{-14}$ s, mean free path, $l_x(260 \text{ K}) = 220 \text{ \AA}$, and if τ is independent of direction, $l_z(260 \text{ K}) = 20 \text{ \AA}$, which is approximately 3 times the layer spacing along the *c* axis (there are three layers per hexagonal unit cell, *c* = 17.76 Å). When electron-phonon interaction dominates scattering as seems to be the case here based on the measured $\rho(T)$, one expects $\tau^{-1} \propto T$. Then, PdCoO₂ would only reach the *c*-axis Ioffe-Regel limit at temperatures of $\sim 600^\circ \text{C}$. However, the Pt compound should be much closer because of its higher anisotropy. Assuming that the in-plane resistivity of the two compounds is similar, the Ioffe-Regel limit for the Pt compound would be near room temperature.

Figure 3 shows the calculated $S(T)$ for the in-plane and *c*-axis directions. The in-plane thermopower is positive, approximately linear in *T* and small in magnitude. The magnitude and *T* dependence are consistent with what might be expected in a good metal. The *c*-axis thermopower is completely different. It has opposite (*n*-type) sign, is large, and saturates at high *T*. In PdCoO₂, $S(T)$ reaches $\sim -200 \mu\text{V/K}$, while for PtCoO₂ it exceeds

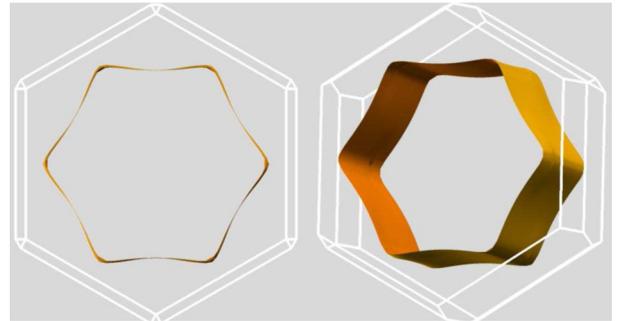


FIG. 2 (color online). Calculated Fermi surface of PtCoO₂ including spin orbit. Γ is at the center.

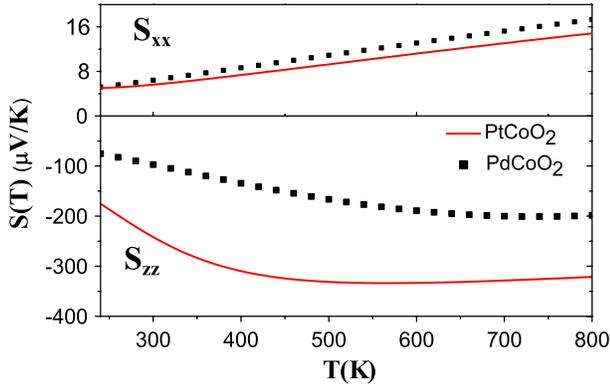


FIG. 3 (color online). Constant scattering time $S(T)$ for PtCoO₂ and PdCoO₂ in-plane and along c . Note the different scales for the two directions.

$-300 \mu\text{V/K}$ in magnitude above 400 K. Hasegawa and co-workers [21] reported measurements of $S(T)$ on ceramic PdCoO₂ finding low values of 2–4 $\mu\text{V/K}$ in the range 100–400 K. While it is not possible to compare this directly with the calculated value without knowledge of the anisotropic thermal conductivity, it is consistent with the low values that we obtain in the high electrical conductivity (in-plane) directions.

The very large values of the thermopower in the c -axis direction would be consistent with practical thermoelectric applications, especially for the Pt compound, although Pt is very expensive. In the present materials it is expected that the thermal conductivity will be anisotropic because there should be a strong electronic contribution in-plane but not in the c -axis direction, assuming that the Wiedemann-Franz relation holds. It will be of interest to measure the thermal conductivity in the c -axis direction to determine the figure of merit, $ZT = \sigma S^2 T / \kappa$ (here σ and κ are the electrical and thermal conductivities), especially from 300 K to higher T , since this is the range where $S(T)$ is high.

This strongly anisotropic thermopower is extremely unusual. At low T the thermopower is given by the Mott formula, $S_{xx}(T) = (\pi^2 K^2 T / 3e) [d \ln(\sigma_{xx}) / dE]_{E=E_F}$ for the x direction and similarly for the other components. In the constant scattering time approximation σ_{xx} is proportional to the integral of the squared band velocity, v_x^2 , over the Fermi surface multiplied by the inverse scattering rate, τ . The finite T formulas [15,19] are similar, but involve Fermi broadening so energy derivative is taken by integrating with $E f'(E)$, where f' is the derivative of the Fermi function, amounting to a broadened version of the derivative operator. The logarithmic derivative means that the scale of the conductivity cancels and what matters is the energy scale on which it is varying. Therefore for doped parabolic band semiconductors, $S(T)$ is isotropic even if the effective mass tensor is extremely anisotropic. In fact while $S(T)$ can be anisotropic, it is generally much more

isotropic than the conductivity at least in materials where the transport is coherent in all directions. Furthermore, for a single half filled band the thermopower is usually low even if the band is narrow. This is because the conductivity is near its maximum as function of band filling and therefore the derivative is small. Finally, it is known that materials with open Fermi surfaces, such as in the present case can have electronlike behavior in one direction and holelike behavior in another, so that opposite sign thermopowers may occur. However the magnitudes in the two directions are still generally similar since the energy scale for variations in the band structure is similar in the different directions.

The strong anisotropy of $S(T)$ in PdCoO₂ and PtCoO₂ comes from band structure effects. $S(T)$ is related to the logarithmic derivative of the conductivity. In Fig. 5 we show the ratio $\sigma_{zz} / \sigma_{xx}$ at 260 K as a function of energy. This ratio is exceedingly low for the actual chemical potential. However, as shown it increases strongly above E_F . The plot is reminiscent of that conductivity of a conventional semiconductor as a function of doping level. Here the chemical potential is pinned in the gap by the fact that the material is actually a high carrier density metal and not a semiconductor. In any case, the origin of this behavior of the conductivity is seen in the band structure. Figure 4 shows the Fermi surface for a 100 meV increase in the Fermi level. This is a relevant energy because the factor $E f'(E)$ in the Boltzmann formula for the thermopower significantly samples energies up to $\sim 5kT$. As may be seen, the warping of the Fermi surface increases strongly, particularly around the corners of the hexagonal shaped Fermi surface. This arises because as seen in Fig. 1 the next higher band anticrosses with the band forming the Fermi surface along this direction. This is k_z dependent yielding a k_z -dependent distortion of the edge of the Fermi surface and the different effective energy scales determining $S(T)$ in different directions.

These may be interesting materials from the point of view of correlated electron behavior. The crystal structure can be described as metallic Pd/Pt sheets with a Pd/Pt distance of 2.83 Å, separated by insulating CdI₂ structure

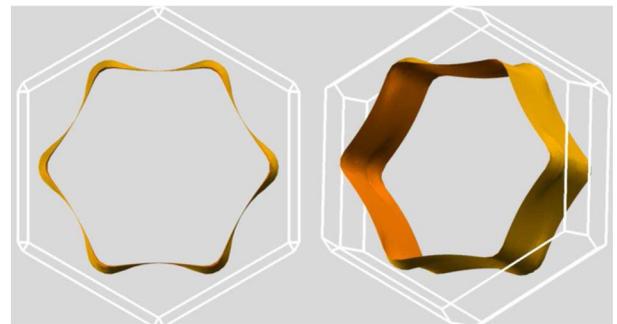


FIG. 4 (color online). Fermi surface of PtCoO₂ as in Fig. 2 but with E_F increased by 100 meV. Note the enhanced three dimensionality along the corners of the hexagonal cylinders.

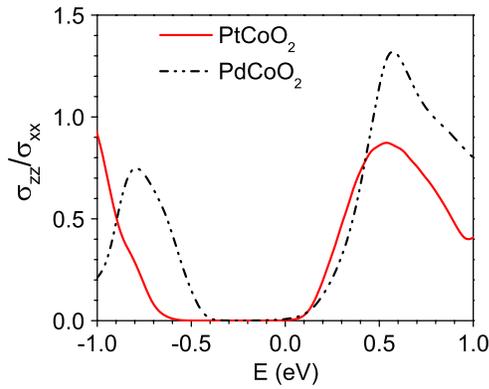


FIG. 5 (color online). Calculated conductivity anisotropy σ_{zz}/σ_{xx} at 260 K as a function of chemical potential, where zero is the stoichiometric value for the compound.

CoO₂ sheets. This CoO₂ structure is effectively insulating at the band structure level, leading to the conductivity anisotropy. The same structure CoO₂ sheets occur in Na_xCoO₂, which has remarkable physical properties. Naively, one may suppose that the insulating CoO₂ should be strongly correlated with local moment magnetism driven by the Coulomb repulsion. This is not the case based on experiment, which points to band insulating behavior, and low spin Co. Nonetheless, a correlated state may be nearby and could manifest itself in transport. We note that Boltzmann theory is very robust for coherent transport. It accurately describes the in-plane thermopower of Na_xCoO₂ at room temperature and above even though the material is near magnetism and possibly influenced by a quantum critical point (the out-of-plane transport is incoherent) [22,23].

To summarize, PdCoO₂ and PtCoO₂ are in a very unusual transport regime. They are highly anisotropic, but still coherent metals. This anisotropy is particularly extreme for PtCoO₂. PdCoO₂ will approach the Ioffe-Regel limit only at high T , but PtCoO₂ may show a crossover in the c -axis direction near room temperature. The thermopowers of these materials are predicted to be very unusual, with very large values along c and small metallic values of opposite sign in-plane. While the unusual transport arises from a detail of the band structures it is chemically robust since both the Pt and Pd compounds have similar behavior. Depending on the thermal conductivity the c -axis direction may have high thermoelectric ZT . Experimental study of $S(T)$ in these compounds may reveal new unanticipated facets of metallic transport.

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