Metal-insulator transition in Ca$_{1-x}$Li$_x$Pd$_3$O$_4$

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Metal-insulator transition in Ca$_{1-x}$Li$_x$Pd$_3$O$_4$ has been studied through charge transport measurements. The resistivity, the Seebeck coefficient, and the Hall coefficient are consistently explained in terms of a simple one-band picture, where a hole with a moderately enhanced mass is itinerant three-dimensionally. Contrary to the theoretical prediction [Phys. Rev. B62, 13426 (2000)], CaPd$_3$O$_4$ is unlikely to be an excitonic insulator, and holds a finite carrier concentration down to 4.2 K. Thus the metal-insulator transition in this system is basically driven by localization effects.

I. INTRODUCTION

A metal-insulator transition is one of the most important topics in solid-state physics. In case of a conventional semiconductor, donors (acceptors) supply electrons (holes) in a band insulator. A metal-insulator transition takes place at a critical carrier density, where the average carrier-carrier distance is comparable with the effective Bohr radius of the doped impurity atom. The critical carrier density has been quantitatively discussed for various semiconductors.

Metal-insulator transitions in strongly correlated systems are completely different from that in a band insulator. The most remarkable example is that in high-temperature superconductors, where the metallic state is accompanied by high temperature superconductivity. As the second example, the colossal magnetoresistive manganites exhibit a peculiar transition where the metallic state is stabilized by ferromagnetism. Actually, there are many types of insulating state (Mott insulator, charge order, and stripes) for strongly correlated systems, and accordingly there are so many ways how these insulating states collapse upon doping, pressure, temperature, and external field.

Since transition-metal oxides are often insulating due to the strong correlation, they can be a good playground for studies of metal-insulator transitions. In this sense, we have paid special attention to CaPd$_3$O$_4$. Figure 1 shows the crystal structure of CaPd$_3$O$_4$ known as a NaPtaO$_4$-type structure. The divalent Pd$^{2+}$ of (4d)$^8$ is surrounded with four O$^{2-}$ anions, and the PdO$_4$ clusters stack one another to form a column. Because of the cubic symmetry, the PdO$_4$ column runs along the x, y, z directions to make a thee-dimensional network.

The first interesting point is that CaPd$_3$O$_4$ shows a metal-insulator transition by substitution of Na for Ca, as was found by Itoh et al.

II. EXPERIMENTAL

Polycrystalline samples of Ca$_{1-x}$Li$_x$Pd$_3$O$_4$ (x=0, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) were prepared by a solid-state reaction aided with NaCl addition. Stoichiometric amount of PdO, CaCO$_3$, and LiCO$_3$ of 99.9% purity were...
thoroughly mixed. NaCl was then added with the mixture in a mass ratio of 2:1, thoroughly mixed again, and fired at 1073 K for 24 h in air. The product was finely ground, and NaCl was rinsed out in hot distilled water. The dried powder was then pressed into pellets, and was sintered in air at 1073 K for 24 h in air. The product was finely ground, and NaCl was rinsed out in hot distilled water.

The samples were characterized through the x-ray diffraction (XRD) with Fe Kα as an x-ray source in a θ–2θ scan mode. The resistivity was measured by a four-terminal method from 4.2 to 300 K in a liquid He cryostat, and from 300 to 700 K in a cylinder furnace in air. The Seebeck coefficient was determined by the data at 4.2 K decreases by four orders of magnitude from $x > 0$ to $x = 0$, all the reflection peaks are indexed as a NaPt$_3$O$_4$-type structure with an a-axis length $a_0$ of 5.74 Å. As is shown in the inset, $a_0$ decreases systematically with $x$, which clearly indicates that Li$^+$ (0.76 Å) and Ca$^{2+}$ (1.00 Å) make a solid solution. For $x = 0.3$, however, a tiny (5%) trace of reduced Pd is observed near $\theta = 51$ deg. The amount of the reduced Pd gradually increases with $x$ for $x > 0.3$, and exceeds 10% for $x > 0.6$.

Figure 3(a) shows the temperature dependence of the resistivity ($\rho$) of the prepared samples. The resistivity changes systematically with $x$, whose magnitude at 4.2 K decreases by four orders of magnitude from $x = 0$ to 0.6. This clearly indicates that the substituted Li supplies carriers into the sample. Towards 0 K, $\rho$ for $x = 0$ divergingly increases while $\rho$ for $x = 0.1$ remains a finite value. This means the metal-insulator transition takes

![FIG. 2: X-ray diffraction pattern of CaPd$_3$O$_4$. (a) $x = 0$, and (b) $x = 0.3$](image)

![FIG. 3: (a) Resistivity, and (b) the Seebeck coefficient of Ca$_{1-x}$Li$_x$Pd$_3$O$_4$](image)

**III. RESULTS AND DISCUSSION**

Figure 2 shows typical XRD patterns of the prepared samples. For $x = 0$, all the reflection peaks are indexed as a NaPt$_3$O$_4$-type structure with an a-axis length $a_0$ of 5.74 Å. As is shown in the inset, $a_0$ decreases systematically with $x$, which clearly indicates that Li$^+$ (0.76 Å) and Ca$^{2+}$ (1.00 Å) make a solid solution. For $x = 0.3$, however, a tiny (5%) trace of reduced Pd is observed near $\theta = 51$ deg. The amount of the reduced Pd gradually increases with $x$ for $x > 0.3$, and exceeds 10% for $x > 0.6$.

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place between \( x = 0 \) and 0.1.

Figure 3(b) shows the temperature dependence of the Seebeck coefficient \((S)\) of the prepared samples. All the Seebeck coefficients are positive, indicating that the majority carrier is a hole in this system. \( S \) for \( x = 0 \) is roughly proportional to temperature below 100 K, which is a hallmark of a conventional metal. In the sense that a finite carrier concentration remains as \( x = 0 \) saturates as \( T \to 0 \), \( \text{CaPd}_3\text{O}_4 \) is essentially a metal. Considering the large thermopower, it would be more appropriate to regard \( \text{CaPd}_3\text{O}_4 \) as a degenerate semiconductor rather than a metal. With increasing \( x \), \( S \) systematically decreases, which indicates that the substituted Li supplies holes to \( \text{Ca}_{1-x}\text{Li}_x\text{Pd}_3\text{O}_4 \). The doped samples also show a similar \( T \)-linear Seebeck coefficient at low temperatures to the \( x = 0 \) sample. At high temperatures for smaller \( x \), the Seebeck coefficient takes a maximum and decreases with increasing temperature. This means that the minority carriers (electrons in this case) are thermally excited, and also means that the band gap of \( \text{CaPd}_3\text{O}_4 \) is smaller than hundreds of K.

Figure 4 shows the temperature dependence of the Hall coefficient \((R_H)\) of the prepared samples. As is similar to the Seebeck coefficient, the sign of the Hall coefficient is positive for all the samples, indicating the majority carriers are holes. The magnitude systematically decreases with increasing \( x \), and \( R_H \)'s for \( x = 0.1 \) and 0.2 are essentially independent of temperature. These results are what is expected in a conventional metal, magnitude of which is inversely proportional to the carrier concentration.

We should note that \( R_H \) for \( x = 0 \) saturates as \( T \to 0 \). This clearly indicates that \( \text{CaPd}_3\text{O}_4 \) is essentially a degenerate semiconductor with a low carrier concentration of \( 10^{19} \text{ cm}^{-3} \), which is consistent with the \( T \)-linear \( S \). Contrary to the theoretical prediction by Hase and Nishihara, \( \text{CaPd}_3\text{O}_4 \) is unlikely to be an excitonic insulator having the charge gap of the order of an exciton binding energy at low temperatures. Thus we conclude that the nonmetallic \( \rho \) for \( x = 0 \) is due to localization effects. \( R_H \) for \( x = 0 \) exhibits remarkable temperature dependence, which implies the existence of the additional carriers activated thermally. This further suggests that the activation energy is smaller than a few tens of K, because \( R_H \) is clearly dependent on temperature down to 10 K. The small activation energy can also explain the 170-K peak in \( S \) for \( x = 0 \), where the thermally activated electrons dominates at high temperatures. It is not surprising that \( R_H \) and \( S \) show different temperature dependences. According to a two-band model consisting of electrons and holes, \( R_H \) and \( S \) are averaged with different weights of electron \((\sigma_e)\) and hole \((\sigma_h)\) conductivities. A more quantitative analysis would be difficult, unless \( \sigma_e \) and \( \sigma_h \) were experimentally determined.

A possible candidate for the small activation energy is the band gap of \( \text{CaPd}_3\text{O}_4 \). According to the intuitive explanation by Doublet et al., the valence band of \( \text{CaPd}_3\text{O}_4 \) consists of \( \text{Pd} \, 4d \), while the conduction band consists of \( \text{Pd} \, 4d \). Owing to the large dispersion of the \( \text{Pd} \, 4d \) band, the energy gap between the valence and conduction bands is expected to be small. In fact, the band calculation showed that \( \text{CaPd}_3\text{O}_4 \) was a semi-metal with zero band-gap.

Now we will make a quantitative discussion on the metal-insulator transition in \( \text{CaPd}_3\text{O}_4 \). As already mentioned, Li substitution supplies holes in \( \text{CaPd}_3\text{O}_4 \), and the doped holes seem “normal”, in the sense that they give the \( T \)-linear Seebeck coefficients and the \( T \)-independent Hall coefficients at low temperature. Thus we employ the simplest formula of \( R_H = 1/ne \), where \( n \) is the hole concentration. Then \( R_H \)'s for \( x = 0.1 \) \((7.7\times10^{-2} \text{ cm}^3/\text{C})\) and \( x = 0.2 \) \((3.7\times10^{-2} \text{ cm}^3/\text{C})\) correspond to 0.08 and 0.16 holes per unit formula, respectively. In spite of the rough estimation, the hole concentration obtained from \( R_H \) is in good agreement with \( x \), and we can roughly assume that the Li content \( x \) supplies \( x \) holes per Li cation.

In the lowest order approximation, the Seebeck coeffi-
cient of a conventional metal is expressed as

\[ S = -\frac{\pi^2 k_B^2 T}{2e E_F} \]

where \( E_F \) is the Fermi energy. Then \( E_F \) can be experimentally determined from the \( T \)-linear part of the Seebeck coefficient as \( E_F = \frac{\pi^2 k_B^2 T}{2e^2 S} [\text{eV}] \). Figure 5(a) shows \( \pi^2 k_B^2 T/2e^2 S \) for the prepared samples. All the data are roughly independent of temperature at 80 K, from which we evaluate \( E_F \) for each sample. We think that \( T/S \) at low temperatures is less reliable, owing to the small magnitude of \( S \) and low sensitivity of the copper-constantan thermocouple below 10 K.

Figure 5(b) shows the evaluated \( E_F \) plotted as a function of \( x \). We further assume a nearly free hole with an effective mass of \( m^* \), the Fermi energy is written as

\[ E_F = \frac{h^2}{2m^*} (3\pi^2 n)^{\frac{2}{3}} = \frac{h^2}{2m} \left( \frac{3\pi^2}{a_0^3} \right)^{\frac{2}{3}} m^* \]

where \( m \) is the bare mass of an electron (Note that a unit cell includes two unit formulae). The dotted and solid curves show the calculated \( E_F \) with \( m^*/m = 4 \) and 6, respectively, between which the evaluated \( E_F \) lies. This means that the effective mass of Ca\(_{1-x}\)Li\(_x\)Pd\(_3\)O\(_4\) is nearly independent of \( x \), and is moderately (4-6 times) enhanced from the bare mass, possibly owing to the 4d nature.

Finally we will make brief comments on remaining issues. (i) Ca\(_{1-x}\)Li\(_x\)Pd\(_3\)O\(_4\) is a possible candidate for a p-type thermoelectric oxide \(^{(10)}\). A thermoelectric material is a material that converts heat into electric power, and electric power into heat, through the thermoelectric phenomena in solids. The thermoelectric power factor \( S^2/\rho \) is 1.6 \( \mu \)W/cm K\(^2\) for \( x = 0.4 \) at 300 K, which is comparable to the value for the polycrystalline NaCoO\(_4\) known as a promising candidate for a thermoelectric oxide \(^{(11)}\). (ii) At present, we have no direct evidence that the doped holes form on-site pairs like Pd\(^{4+}\). The charge transport observed in the present paper is quantitatively explained in terms of nearly free holes with the enhanced mass. In other words, this system is highly robust against charge disproportionation and/or charge density wave. The orthogonally entangled PdO\(_4\) columns may play an important role, as was suggested by Doublet et al.\(^{(9)}\). Another reason would be that the carrier concentration was too low to observe the “valence skipper” effects. In the case of Bi oxides, the valence skipper effects are most remarkable in BaBiO\(_3\), where the charge ordered state of Bi\(^{3+}\) and Bi\(^{5+}\) are stabilized. With doping, the Bi\(^{3+}\)–Bi\(^{5+}\) state collapses and the band picture gradually recovers. In the present study, the Pd\(^{4+}\) content is less than 10%, and this corresponds to BaPb\(_{1-x}\)Bi\(_x\)O\(_{2+}\)(\( x < 0.2 \)) which can be explained by the band picture \(^{(12)}\). Thus it would be more tempting to synthesize a Pd oxide consisting of (formally) Pd\(^{3+}\) to search for the valence skipper effects. (iii) The small band gap implies that electrons can be doped in the conduction band. Preliminarily we succeeded in electron doping by substitution of a trivalent ion (La\(^{3+}\), Y\(^{3+}\), and Bi\(^{3+}\)) for Ca\(^{2+}\). (iv) The present results are quite different from \( \rho \) and \( S \) for Ca\(_{1-x}\)Na\(_x\)Pd\(_3\)O\(_4\) by Itoh et al.\(^{(4, 5)}\). We prepared Na substituted samples, but found that \( \rho \) and \( S \) were essentially the same as those for Ca\(_{1-x}\)Li\(_x\)Pd\(_3\)O\(_4\). We employed “NaCl flux” technique to suppress reduction of PdO, but Itoh et al. used conventional solid state reaction. Thus the different preparation method might give different samples.

**IV. SUMMARY**

The resistivity, the Seebeck coefficient, and the Hall coefficient for Ca\(_{1-x}\)Li\(_x\)Pd\(_3\)O\(_4\) (\( x = 0.6 \)) have been measured and analyzed. Since the parent material CaPd\(_3\)O\(_4\) is a degenerate semiconductor with a finite carrier concentration of 10\(^{19}\) cm\(^{-3}\), it is unlikely to be an excitonic insulator as suggested by Hase and Nishihara \(^{(13)}\). The metal-insulator transition in this system is thus basically driven by localization effects. The carrier concentration dependence of the Hall and Seebeck coefficients is consistently explained in terms of a simple one-band picture, where a hole with a moderately enhanced mass \( (m^*/m \sim 4-6) \) is itinerant three-dimensionally.

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[1] N. F. Mott, *Metal-insulator transition* 2nd ed. (Taylor & Francis, London, 1990).
[2] D. Belitz and T.R. Kirkpatrick, Rev. Mod. Phys. 66, 261 (1994).
[3] M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[4] K. Itoh, Y. Yano and N. Tsuda, J. Phys. Soc. Jpn. 68, 3022 (1999).
[5] K. Itoh and N. Tsuda, Solid State Commun. 109, 715 (1999).
[6] I. Hase and Y. Nishihara, Phys. Rev. B62, 13426 (2000).
[7] C. M. Varma, Phys. Rev. Lett. 61, 2713 (1988).
[8] R. C. Wnuk, T. R. Touw, and B. Post, IBM J. Res. Dev. 8, 185 (1964).
[9] M.-L. Doublet, E. Canadell, and M.-H. Whangbo, J. Am. Chem. Soc. 116, 2115 (1994).
[10] G. D. Mahan, Solid State Physics 51, 81 (1979).
[11] I. Terasaki, Y Sasago and K. Uchinokura, Phys. Rev. B56, R12685 (1997).
[12] S. Uchida, K. Kitazawa and S. Tanaka, Phase Tans. 8, 95 (1987).