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Pressure effect on Charge-Density-Wave in $Per_2M(mnt)_2$ (M=Pt, Au)

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Abstract

The Charge-Density-Wave (CDW) transition temperature T_{CDW} of quasione-dimensional conductors $Per_2M(mnt)_2$ (M=Au, Pt) steeply decreases with increasing pressure up to 0.5 GPa but the pressure-induced transition to a metallic state is not observed at least up to 1.5 GPa. At ambient pressure the resistance decreases with decreasing temperature but turns to increase at the temperature T_{min} corresponding to the resistance minimum, and then it exponentially raises below T_{CDW} . T_{min} initially decreases steeply with increasing pressure but becomes nearly constant at pressures above 0.5 GPa, where T_{CDW} disappears. Nonlinear conduction is observed under pressures above 1 GPa and at temperatures below 4.2 K. The present results are discussed in terms of the pressure-induced quantum melting of the CDW state. © 2005 Elsevier Ltd. All rights reserved.

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1. Introduction

There has been of great interest in the exotic phases that are expected between ordered and disordered phases as one tunes the interactions in systems using some control parameter such as magnetic field H and pressure P other than temperature T. When the competing interactions in the material are tuned at low temperature, quantum mechanical nature is expected to be observed in the process in which ordered phases collapse into disordered phases. In fact, a vortex liquid phase in the H-T phase diagram for superconductors [1], 'quantum liquid crystal' phase between the charge-stripes ordered and high- T_c superconducting phases [2] and pressure-induced melting of the Charge-Density-Waves (CDW) state [3] are reported. Here, we focus on materials that undergo the CDW transition at low temperatures and investigate the pressure effects of the CDW state to examine the possible existence on quantum effect on the process in a collapse of the CDW state.

The materials that we focused on are $Per_2Pt(mnt)_2$ and $Per_2Au(mnt)_2$. These compounds are quasi-one-dimensional conductor that undergo the CDW transition at 8 and

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12 K for M=Pt and Au, respectively [4]. The CDW formation has been confirmed based on diffuse X-ray studies [5] and measurement of nonlinear conduction [6]. The metallic properties are associated with the existence of stacks along the *b* axis of perylene molecules $(Per)_2^+$. The counterions $M(mnt)_2^-$ also form stacks along the *b* axis. However, they do not contribute to the electrical conductivity but play a key role in the magnetic properties [7]. For M=Au, there is no magnetic moment (S=0), while for M=Pt, the M(mnt)₂ units form chains of localized S=1/2 spins, leading to a spin-Peierls transition [4]. Thus, two compounds are good materials to examine quantum melting of the CDW state, including a role of spin interaction.

2. Experiments

Single-crystal samples were grown by electro-crystallization method described previously [8]. Typical crystal dimensions used for measurements were of order $2 \times 0.05 \times$ 0.02 mm^{-3} , where the long axis is the *b*-axis. For each sample, the resistance and current–voltage (*I–V*) characteristics were measured along the *b*-axis using a standard dc four-probe configuration. Electrical contacts were prepared by evaporating gold (Au) in a vacuum. The electrical leads, 20 µm Au wires, were glued with platinum paste on the evaporated Au contacts. All measurements were carried out under the current-controlled bias. The resistance is

measured in the temperature range of 1.4–300 K. External pressure up to 1.6 GPa were generated by using a conventional clamp-typed pistoncylinder pressure-cell. Nearly hydrostatic pressure was produced in the teflon cell filled with a fluid pressure-transmitting medium of the Daphne oil 7373 [9].

3. Results and discussions

We measured the T-dependence of resistance under various pressures for six samples of Per₂Pt(mnt)₂. Fig. 1 shows the typical T-dependence of resistance under various pressures for sample A8. At ambient pressure, the roomtemperature resistivity is ρ (300 K) = 1.5 × 10⁻³ [Ω cm] and the metallic T-dependence of resistance turns into the nonmetallic one at ~ 20 K. As temperature decreases below the temperature corresponding the resistance minimum, $T_{\rm min}$ the metal-insulator transition temperature due to CDW formation is observed at $T_{CDW} = 8$ K where is a temperature corresponding to a peak in the slope $d\ln R/d(1/T)$. Below $T_{\rm CDW}$ the resistance significantly increases, but cannot be described by a single exponential behavior. As a consequence, the gap (Δ) can only be crudely estimated as $\Delta/k_B = 100$ K using the activation law, $R \sim \exp[-\Delta/k_B T]$. These results are in overall good agreement with that reported earlier [10]. As pressure increases up to ~ 0.4 GPa, T_{\min} and T_{CDW} decrease but the resistance at low temperatures is approximated by the activation law. In this pressure range the insulating state due to CDW formation is observed as well as that at ambient pressure. Above 0.5 GPa, however, the resistance gradually increases with decreasing temperature and the resistance is hardly



Fig. 1. Temperature dependence of resistance under various pressures for sample A8 of $Per_2Pt(mnt)_2$.

described by an exponential behavior. The peak in $d \ln R/d(1/T)$ becomes ambiguous. The value Δ/k_B estimated 0.43 GPa is ~4 K, which is comparable to $T_{\rm CDW}$ (~5 K). These results show that the non-metallic state observed above ~0.5 GPa is not due to CDW formation. In order to investigate origins of the non-metallic state above ~0.5 CPa, we focus on parameters of $T_{\rm min}$ and $T_{\rm CDW}$ as a function of P which characterize the T-dependence of resistance in Per₂Pt(mnt)₂.

Fig. 2 shows the *P*-dependences of T_{\min} and T_{CDW} obtained for six samples of Per₂Pt(mnt)₂. Although their values vary from sample to sample, the P-dependences of T_{\min} and T_{CDW} are in overall systematic. As pressure increases, T_{\min} initially decreases steeply and becomes nearly constant against pressure above ~ 0.5 GPa. On the other hand, T_{CDW} monotonously decreases with increasing pressure and disappears at ~ 0.5 GPa, which is comparable to the pressure corresponding to the remarkable change in the *P*-dependence of T_{\min} . Thus, pressure-induced collapse of the CDW state is observed at ~ 0.5 GPa. The nonmetallic state is observed over a wide pressure range of 0.5-1.3 GPa, but no pressure-induced transition to a metallic state is observed. In fact, the critical pressure P^* of pressure-induced CDW-to-metal transition has been reported to be over 2 GPa in other CDW systems such as TiSe₂ ($P^* \sim 2.5$ GPa) [3], NbSe₃ ($P^* \sim 2.4$ GPa) [11] and Lu₅Ir₄Si₁₀ ($P^* \sim 2.1$ GPa) [12]. Also in Per₂Pt(mnt)₂ the metallic transition is expected to be appeared at pressure over 2 GPa, hence this non-metallic state can be accepted as an intermediate one between CDW and metal states.

Fig. 3 shows the *T*-dependence of resistance under various pressures for four samples of $Per_2Au(mnt)_2$.



Fig. 2. Pressure dependences of $T_{\rm CDW}$ (open symbols) and $T_{\rm min}$ (closed symbols) obtained for six samples of Per₂Pt(mnt)₂. Broken lines are guides to the eye.



Fig. 3. Temperature dependences of resistance under various pressures for four samples of Per₂Au(mnt)₂.

At ambient pressure the value of the room temperature resistivity is ρ (300 K)=1.0×10⁻³ (Ω cm) and the resistance minimum and the metal-insulator transition due to CDW formation are observed at $T_{\rm min} = 18$ K and at $T_{\rm CDW} = 12$ K, respectively. The *T*-dependence of resistance is in overall good agreement with that reported earlier [4] [10]. Although the T-dependence of resistance under pressures varies from sample to sample, the metal-insulator transition due to the CDW formation is observed and the resistance exponentially increases with decreasing temperature under pressures below 0.3 GPa. Above 0.7 GPa the resistance gradually increases with decreasing temperature, which cannot be described by the exponential behavior. The non-metallic state remains even at high pressure above 1.5 GPa but no transition to the metallic state is observed. Thus, we find that the T-dependence of resistance under pressures in Per₂Au(mnt)₂ is fundamentally the same as that in Per₂Pt(mnt)₂. This similarity shows that the pressureinduced collapse of the CDW state is determined by the metallic properties in the Per₂ chains, but no spin interaction in the $Pt(mnt)_2$ chains contribute to it.

Figs. 4 and 5 show the *I*–*V* characteristics in the nonmetallic state above 1 GPa and below 4.2 K for sample A14 of Per₂Pt(mnt)₂ and for sample BA4 of Per₂Au(mnt)₂, respectively. Both samples exhibit nonlinear *I*–*V* characteristics with a threshold voltage, which is very similar to a typical CDW conduction. This similarity suggests nonlinear conduction due to the CDWs motion. However, such a nonlinear conduction generally has been observed below T_{CDW} , i.e. in the ordered CDW state. In fact, the nonlinear conduction of Per₂Pt(mnt)₂ and Per₂Au(mnt)₂ at ambient pressure is observed below T_{CDW} but never above T_{CDW} [6]



Fig. 4. I-V characteristics for sample A14 of Per₂Pt(mnt)₂ (P=1.0 GPa, T=4.2 K).

[10]. The values of the threshold electric-field *E*th are estimated as $\sim 50 \text{ (mV/cm)}$ for M=Pt and $\sim 30 \text{ (mV/cm)}$ for M=Au, which are more than one order smaller than that observed in the CDW state at ambient pressure by Lopes et al. [7]. These results strongly suggest that the nonlinear conduction with the small value of *E*th is associated with the CDW motion, but not due to CDWs sliding in the ordered state.

A simple description of the ordered CDW state for real materials is one that consists of bundles of onedimensional CDW chains in which neighboring CDW



Fig. 5. I-V characteristics for sample BA4 of Per₂Au(mnt)₂ (P=1.6 GPa, T=1.5 K).

chains are arranged in the phase difference of π due to the Coulomb interactions, that is, three-dimensional lattice of CDWs with long-range order is formed as well as a crystal structure. Nonlinear conduction due to CDWs sliding is generally observed in this crystal state, in which high external electric field needs to start CDWs motion for the crystal stiffness, especially at low temperatures. On the other hand, in the vicinity of P^* CDW fluctuations increase with increasing pressure and the CDW state loses long-range order, leading to melting of the CDW state. In this case, the value of Eth will decrease with losing the crystal stiffness. When the melting is driven near $T \sim 0$ K, the melting process is expected to exhibit quantum mechanical in nature, as reported in the vortex lattice [1] and two-dimensional CDW crystal [3]. The situation above 1 GPa and below 4.2 K in $Per_2M(mnt)_2$ (M=Pt, Au) is expected to correspond to this case, where the value of Eth is quite small. However, more studies need to make clear quantum nature in the melting process of the CDW state. Studies of the P- and T-dependences of the nonlinear conduction and confirmation of P^* are underway.

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