Theory of Unconventional Charge Ordering and Electrical Transport in Skutterudite PrRu$_4$P$_{12}$

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Abstract. The unconventional properties of charge ordering associated with the metal-insulator transition in skutterudite PrRu$_4$P$_{12}$ are studied theoretically. It is demonstrated by a simplified model Hamiltonian that the electrical transport in the charge ordered state is governed by a large $f$-orbital fluctuation. In particular, the mechanism of an anomalous temperature dependence of the Hall conductivity is discussed in detail. The nature of residual magnetic interaction giving magnetoresistance at low temperature is also discussed.

1. Introduction
The rare-earth filled skutterudite compounds with the general formula RT$_4$X$_{12}$ exhibit a remarkable variety of phase transitions [1]. Among them, charge ordering associated with the metal-insulator transition in PrRu$_4$P$_{12}$ has been attracting great interest due to its unconventional properties [2]. Recent neutron scattering experiments for PrRu$_4$P$_{12}$ by Iwasa et al. have revealed that a strong and characteristic temperature dependence of the $f$-electron crystal field (CF) levels is realized in the charge order phase [3]. In the normal phase above the transition temperature $T_c = 63$K, all Pr ions are equivalent and singlet $\Gamma_1$ becomes the ground state in the CF level scheme. With lowering temperature below $T_c$, the excitation energy to a triplet $\Gamma_4$ is reduced in one of the sublattices, and level crossing with the singlet takes place at 40K. As a result, two distinct CF ground states, singlet and triplet, are realized in different sublattices at zero temperature. Apparently, this fact and other subsequent experimental results indicate importance of an interaction between conduction electrons and localized $f$ electrons in the charge order formation. In this report, we review recent theoretical progress on the stability mechanism and electrical transport in the charge order phase of PrRu$_4$P$_{12}$ [4, 5, 6]. Then, we also discuss the origin of anomalous magnetic properties at low temperature.

2. Model Hamiltonian
It has been pointed out that the conduction electron state of PrRu$_4$P$_{12}$ in the normal phase is rather simple since it is composed of a single band with almost half-filling [7]. The so-called $a_u$ band is well approximated by the tight-binding model for the bcc lattice, whose half-filling condition leads to the particle-hole symmetry and a nested Fermi surface.

Considering these facts together with the $f$-electron states, we introduce a simplified
Hamiltonian:

$$H = \sum_{k\sigma} \epsilon_k c^\dagger_{k\sigma} c_{k\sigma} - J \sum_i n_{i\sigma} \phi_i + H_f. \quad (1)$$

In the first term, $c^\dagger_{k\sigma}$ ($c_{k\sigma}$) represents conduction electron creation (annihilation) operators with momentum $k$ and spin $\sigma$. We denote the band dispersion $\epsilon_k$, assuming a complete nesting property $\epsilon_{k+Q} = -\epsilon_k$ for arbitrary $k$. In this study, we assume a parabolic density of states for the conduction band due to analytical simplicity, $\rho_0(\epsilon) = \frac{2}{\pi D^2} \sqrt{D^2 - \epsilon^2}$, where we take $D = 1$ to be the unit of all energies. The second term in eq. (1) represents charge interaction between conduction and $f$ electrons; $n_{i\sigma} = c^\dagger_{i\sigma} c_{i\sigma}$ is the number of conduction electrons at $i$-th lattice site. The occupation of $f$ states is described as $\phi = 1$ when one of the triplet states are occupied and $\phi = 0$ when the singlet state is occupied. Note that this variable is nothing but a hexadecapole moment with the $\Gamma_1$ representation in the singlet-triplet subspace [8, 9]. In addition, we take into account the $f$-electron part in $H$ as

$$H_f = \Delta_0 \sum_i \phi_i + \sum_{ij} K_{ij} \phi_i \phi_j. \quad (2)$$

In the first term, $\Delta_0(>0)$ is the bare CF potential leading to a singlet ground state in the normal phase. The second term represents an inter-site interaction of $f$ electrons.

Throughout this paper, we shall fix the interaction parameters as $J = 0.2$, $K_{ab} = 0$ and $K = K_{aa} = K_{bb} = 0.035$. Hereafter, we discuss the dependences of the transport properties on the CF splitting, for which an effective value $\Delta$ with fixed $J$ and $K$ is used instead of the bare value $\Delta_0$, where $\Delta = \Delta_0 - J - 3/4K$. This is nothing but the splitting in the high-temperature limit where $\phi = 3/4$.

3. Formulation of CPA

We consider a charge ordered state in the model Hamiltonian. Let us define order parameters in $a$ and $b$ sublattices, as $\phi_{a(b)} = \langle \phi_i \rangle$ and $n_{a(b)} = \sum_i \langle n_{i\sigma} \rangle$ for $i \in a(b)$, where $\langle \cdot \rangle$ indicates the thermal average of an operator $\cdot$. At zero temperature, one has saturated occupations $\phi_a = 1$ and $\phi_b = 0$, which result in modulating charge density as $n_a = 1 + \delta q$ and $n_b = 1 - \delta q$ with $\delta q > 0$ in the case of $J > 0$. It is not difficult to determine these order parameters by the Hartree-Fock mean-field (MF) treatment.

Here, we shall study the transport properties determined by the thermal fluctuation of the order parameters. For this purpose, we employ the coherent potential approximation (CPA) which is equivalent to the dynamical mean field theory (DMFT) for given $\phi_a$ and $\phi_b$ [10]. In the framework of the CPA, we introduce two distinct local self-energies at $a$ and $b$ sites, $\Sigma_a(z)$ and $\Sigma_b(z)$, which contain the effect of thermal fluctuation of $f$ orbitals as well as the static MF contribution. Then, the Green’s functions of conduction electrons in the charge ordered state are derived as,

$$G_k(z) = \langle c_{k\sigma}^\dagger c_{k\sigma} \rangle_z = \left( z - \epsilon_k + \mu - \Sigma_f(z) - \frac{\Sigma_a(z)^2}{z + \epsilon_k + \mu - \Sigma_f(z)} \right)^{-1} \quad (3)$$

$$\tilde{G}_k(z) = \langle c_{k\sigma}^\dagger c_{k+Q\sigma} \rangle_z = (z + \epsilon_k + \mu - \Sigma_f(z))^{-1} \Sigma_a(z) G_k(z). \quad (4)$$

Here, $\Sigma_f(z)$ and $\Sigma_a(z)$ stand for the uniform and staggered self-energies $\Sigma_f(z) = (\Sigma_a(z) + \Sigma_b(z))/2$. Since the self-energies should be reduced to the MF values at zero temperature, a gapped quasi-particle spectrum is derived from these Green’s functions.

In the spirit of the CPA, the self-energies should be determined so as to eliminate the average scattering due to local potentials. Such a condition for a site results in

$$\Sigma_a(z) = -J \phi_a - \Sigma_a(z) F_a(z)(J + \Sigma_a(z)), \quad (5)$$
where \( F_a(z) = 1/N \sum_k (G_k(z) + \tilde{G}_k(z)) \) with \( N \) being the number of lattice sites, and the corresponding equation for \( b \) site is given by a replacement \( a \leftrightarrow b \). Thus, one can set up the equations for \( \Sigma_a(z) \) and \( \Sigma_b(z) \), which are coupled with each other through the expressions \( F_{a(b)}(z) \). The CPA equations can be solved by a numerical iteration for input parameters, \( J \), \( \phi_a \), and \( \phi_b \). Although the full DMFT framework requires a self-consistent treatment of \( \phi_a \) and \( \phi_b \), we here use the MF results for such \( f \)-electron parts, to study a qualitative feature of the fluctuation correction to the conduction-electron Green’s function.

\[ \text{Figure 1. Temperature dependence of diagonal conductivity for various CF splittings } \Delta = 0.005 \sim 0.055 \text{ from top to bottom in the high-temperature region.} \]

\[ \text{Figure 2. Temperature dependence of Hall conductivity for various CF splittings } \Delta = 0.005 \sim 0.055 \text{ from top to bottom in the low-temperature region.} \]

4. Transport Properties

Here, we shall study the temperature dependence of diagonal and off-diagonal conductivities in the charge order phase. These conductivities are derived by the linear response theory, in which the current vertex corrections are neglected in the framework of the DMFT [5].

The diagonal conductivity calculated by the CPA are plotted in Fig. 1 as a function of temperature for various values of \( \Delta \). It is apparent that the charge ordering transition at \( T_c \) gives rise to a distinct gap formation showing \( \sigma_{xx} \rightarrow 0 \) as \( T \rightarrow 0 \). One can find a characteristic structure at low temperatures for larger \( \Delta \), which should be a consequence of the densities of states renormalized due to strong \( f \)-orbital fluctuation.

Next, we study the Hall conductivity \( \sigma_{xy} \), which can be induced by a simultaneous application of electric and magnetic fields along \( x \) and \( z \) axes, respectively. The numerical results derived from the CPA are presented as a function of temperature in Fig. 2. One can find that the conductivity is rather small although finite nearly above the transition temperature. It is because the particle-hole symmetry is approximately preserved around the Fermi level in the normal phase due to weak fluctuation.

It might be expected that the conductivity is suppressed for \( T < T_c \) due to the gap formation, as in \( \sigma_{xx} \). Contrary to this expectation, one can find that the magnitude is strongly enhanced in the intermediate-temperature region in the phase and becomes vanishing at zero temperature. It is also apparent that the sign changes as \( \Delta \) varies. These features are reasonably understood based upon the properties of the quasi-particle states. According to the CPA analysis on the density of states, the gap-edge states suffer most severely from \( f \)-orbital fluctuation, and consequently a distinct particle-hole symmetry breaking appears in the low-energy excitations.
A careful analysis has also shown that changing $\Delta$ gives rise to changing the nature of fluctuation, resulting in switching the role of particles and holes. Thus, the unexpected enhancement and the sign change of $\sigma_{xy}$ in the charge order phase are naturally interpreted as a consequence of the fluctuation-induced particle-hole symmetry breaking.

It has been shown experimentally for PrRu$_4$P$_{12}$ that the Hall coefficient $\sigma_{xy}/(H\sigma_{xx}^2)$ is extremely small for $T > T_c$ while it is suddenly enhanced for $T < T_c$ [11]. In addition, it exhibits a distinct sign change in an intermediate temperature. These features of the observation are quite consistent with the present theoretical result.

5. Magnetic Properties at Low Temperature
In the charge order phase, there is no indication of magnetic phase transition down to 50 mK, in spite of remaining triple degeneracy in one of the sublattices. Quite recently, we have studied this issue by analyzing the realistic hybridization process between conduction band and $f$ orbital in both the $jj$-coupling and the $LS$-coupling schemes for $f$-electron states [6]. Then, we have found that a characteristic orbital dependence of the hybridization leads to a distinct difference of the interaction strengths. It is shown that the effective magnetic interaction derived from the hybridization is an order of magnitude smaller than the charge interaction. This is certainly consistent with the simplified model (1) and (2) ignoring any magnetic interaction.

To be precise, however, there is an implication of an effect of the small magnetic interaction in the transport phenomena of PrRu$_4$P$_{12}$. For example, the resistivity at low temperature is strongly suppressed by applying a weak magnetic field, depending on the field direction [11]. These behaviors can be explained by an idea that the field restores a disordered triplet state to the ferromagnetic metallic state. A theoretical study of such a large magnetoresistance based on this idea is now being under progress.

6. Summary
In this paper, the nature of an unconventional charge order in skutterudite PrRu$_4$P$_{12}$ was studied theoretically. We introduced a simplified model Hamiltonian with relevant $f$-electron crystal field levels and calculated the solutions of the coherent potential approximation. It was shown that a large $f$-orbital fluctuation due to singlet-triplet level crossing is very important in understanding the mechanism of transport properties. A possible origin of magnetic properties at low temperature was briefly discussed.

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References
[1] See for example, Proceedings of Skutterudite 2007: J. Phys. Soc. Jpn. 77 Supplement.
[2] Sekine C, et al. 1997 Phys. Rev. Lett. 79 3218.
[3] Iwasa K, et al. 2005 Phys. Rev. B 79 024414.
[4] Shiina R 2008 J. Phys. Soc. Jpn. 77 083705.
[5] Shiina R 2009 J. Phys. Soc. Jpn. 78 104722.
[6] Shiina R and Shiba H 2010 J. Phys. Soc. Jpn. 79 044704.
[7] Harima H and Takegahara K 2003 J. Phys. Condens. Matter 15 S2081.
[8] Shiina R 2004 J. Phys. Soc. Jpn. 73 2257.
[9] Takimoto T 2006 J. Phys. Soc. Jpn. 75 034714.
[10] Freericks J K and Zlatic V 2003 Rev. Mod. Phys. 75 1333.
[11] Saha S R, et al. 2009 Rhys. Rev. B 80 014433.