Anomalous Metal-insulator Transition in Filled Skutterudite $CeOs_4Sb_{12}$

Yoshiki IMAI, Keitaro SAKURAZAWA and Tetsuro SASO

Department of Physics, Saitama University, Saitama 338-8570

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Anomalous metal-insulator transition observed in filled skutterudite $CeOs_4Sb_{12}$ is investigated by constructing the effective tight-binding model with the Coulomb repulsion between f electrons. By using the mean field approximation, magnetic susceptibilities are calculated and the phase diagram is obtained. When the band structure has a semimetallic character with small electron and hole pockets at Γ and H points, a spin density wave transition with an ordering vector $\mathbf{Q} = (1, 0, 0)$ occurs due to the nesting property of the Fermi surfaces. Magnetic field enhances this phase in accord with the experiments.

KEYWORDS: filled-skutterudite compounds, $CeOs_4Sb_{12}$, field induced metal-insulator transition

Filled-skutterudite compounds RM_4X_{12} (R: rare earth; M: Fe, Ru, and Os; and X: P, As, and Sb) with the unique body-centered cubic structures have attracted much interest due to a wide variety of physical phenomena associated with them, e.g., magnetic and quadrupole ordering, Kondo insulating behavior, unconventional superconductivity, etc.[1,2]

Recently, an anomalous phase transition from a paramagnetic metal (PM) to a spin density wave (SDW) state was found at T =0.8 K in $CeOs_4Sb_{12}$. Surprisingly, the phase boundary is shifted to higher temperatures by applying an external magnetic field.[2,3] Such increases in the transition temperature have often been observed in systems with quadrupole-ordering,[4] but the magnetic measurement[5] suggests that the crystal-field (CF) ground state of an f electron is Γ_7, which has no quadrupole moment. Further, the specific heat measurement[2] shows only a small entropy change at the transition, excluding local moment ordering but suggesting SDW or CDW transitions with an opening of a gap over a small portion of the Fermi surfaces of itinerant electronic states. The neutron scattering experiment[6] was performed, but the CF was not clearly observed. The NQR measurements[7] indicate a first-order transition since hysterisis was observed, but the specific heat data[2] clearly show a peak at the transition, indicating a second order transition with some short range order.

$CeOs_4Sb_{12}$ shows semiconducting behavior in the resistivity experiment with a small charge gap ($E_g \sim 10$K) at low temperatures.[5] The overall structure of the optical conductivity and its temperature dependence show behaviors similar to those of $CeRu_4Sb_{12}$, which exhibit a pseudo-gap and mid-infrared peak with a strong temperature dependence.[8,9] Although the band structure of $CeOs_4Sb_{12}$ obtained by the band calculation is quite similar to that of $CeRu_4Sb_{12}$,[10] $CeOs_4Sb_{12}$ exhibits semiconducting behavior, whereas $CeRu_4Sb_{12}$ is experimentally observed to exhibit metallic behavior.[5]

In this letter, we construct an effective model with the characteristic feature of the filled skutterudite compound $CeOs_4Sb_{12}$ and investigate the anomalous metal-insulator transition observed in this material.

The basic crystal structure of filled skutterudites is comprised of X_{12} clusters, occupied with R in the center, that form the body-centered cubic (BCC) lattice. The f orbitals of rare-earth atoms strongly hybridize with the p orbitals in X_{12} clusters close to the Fermi level. The X_{12} cluster has a T_h symmetry, but its effect on the $J = 5/2$ f^1 state in Ce is the same as O_h.

In order to investigate the properties of Ce skutterudites, we previously proposed a simplified tight-binding band model for $CeRu_4Sb_{12}$ consisting of a single valence band and seven f states with spin-orbit interaction; this was considered in the presence of a cubic crystalline field.[11] The single valence band is made up of p orbitals on X_{12} clusters; it has an A_u symmetry, which hybridizes with the f-state in the cluster center. The Coulomb interaction was equally introduced to all the bands in order to make the use of the dynamical mean-field approximation possible.

Here, we simplify the model further to investigate the magnetic properties of $CeOs_4Sb_{12}$. The present model consists of a single f band (representing the $J = 5/2$, Γ_7 ground states) and a single valence band (the above mentioned A_u band), hybridizing with each other. Then Hamiltonian is given by

$$\begin{aligned} H &= \sum_{\mathbf{k},\sigma} \epsilon^c_{\mathbf{k}} c^\dagger_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma} + \sum_{\mathbf{k},\sigma} \epsilon^f_{\mathbf{k}} f^\dagger_{\mathbf{k},\sigma} f_{\mathbf{k},\sigma} \\ &+ \sum_{\mathbf{k},\sigma} \left(V c^\dagger_{\mathbf{k},\sigma} f_{\mathbf{k},\sigma} + h.c \right) + U \sum n^f_{i\uparrow} n^f_{i\downarrow} \\ &+ B_{\rm ext} \sum_{\mathbf{k},\sigma} \sigma \left(n^c_{\mathbf{k},\sigma} + \beta n^f_{\mathbf{k},\sigma} \right) \end{aligned} \quad (1)$$

where $c^\dagger_{\mathbf{k},\sigma}(f^\dagger_{\mathbf{k},\sigma})$ creates a conduction (f) electron with momentum $\mathbf{k}$ and pseudo-spin σ (representing Γ_7 doublet), and $n^f_{i\sigma}$=$f^\dagger_{i,\sigma} f_{i,\sigma}$ with the site index i. We have assumed a BCC tight-binding band with nearest and next-nearest hopping for conduction band, $\epsilon^c_{\mathbf{k}} = \alpha_c t_{\mathbf{k}}$, where $t_{\mathbf{k}} = \cos(k_x a/2)\cos(k_y a/2)\cos(k_z a/2) + \alpha_2[\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]$. The lattice constant a is set equal to unity in the following. α_c and α_2 determine the hopping amplitude. The f state is assumed to exhibit dispersion $\epsilon^f_{\mathbf{k}} = E_f + \alpha_f t_{\mathbf{k}}$, namely, the dispersive part is proportional to $\epsilon^c_{\mathbf{k}}$ but with a small coefficient α_f. This would

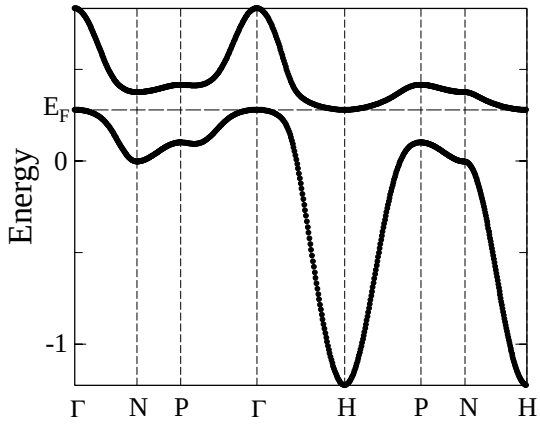

Fig. 1. The band structure for the non-interacting system in the absence of the external field, where α_c=1.0, α_f = 0.03, α_2 = 0.07, $E_f = 0.3$, and $V = 0.15$. E_F represents the Fermi level.

be a reasonable choice since both X_{12} and R occupy the same BCC sites. V is the hybridization between conduction and f electrons. Its $\mathbf{k}$-dependence is neglected. These choices of our model band immensely facilitate the calculations for the strong correlation, which will be reported in a separate paper.[12] Actually, it is obvious that the f-dispersion is created through the X_{12} clusters such that it must be self-consistently determined with $\epsilon^c_{\mathbf{k}}$ and the hybridization $V_{\mathbf{k}}$. U is the Coulomb repulsion between f electrons. It is well-known that $\epsilon^c_{\mathbf{k}}$ and $\epsilon^f_{\mathbf{k}}$ have perfect nesting characters for $\alpha_2 = 0$, $V = 0$, and at half-filling. The last term in eq. (1) represents the Zeeman energy, where $B_{\rm ext}$ denotes the external magnetic field along the z direction and β is the coefficient of effective magnetic moment, which corresponds to $g_J\langle J^f_z\rangle$=6/7×5/6=5/7 for Ce.

Without the Coulomb interaction, the diagonalized energy dispersions are obtained as $E^{\pm}_{\mathbf{k}} = [\epsilon^c_{\mathbf{k}} + \epsilon^f_{\mathbf{k}} \pm \{(\epsilon^c_{\mathbf{k}} - \epsilon^f_{\mathbf{k}})^2 + 4V^2\}^{1/2}]/2$, which are the so-called hybridized bands, but since $\epsilon^f_{\mathbf{k}}$ also has a finite dispersion, the two bands can have a finite overlap if α_f is not too small.

Considering the empirical trend of the lattice constant and the energy gap of Ce-skutterudites, $CeOs_4Sb_{12}$ must be a semimetal.[2] Our assumed band structure is shown in Fig. 1; it has a semimetallic character: the top of the lower band (Γ point) and the bottom of the upper band (H point) are in slight contact with the Fermi level. The overlapping of the bands is about $0.001\alpha_c$.

Although our band structure is quite simplified, Fig. 1 captures the low-energy structure of the band calculation for $CeOs_4Sb_{12}$[10] rather well. In the published band calculation,[10] one of the bands comprised of Γ_8 states exhibits a minimum at the Γ point and is almost in contact with the valence band, but it is neglected in this case. Also, only the single valence band is taken into account and the lower bands are completely neglected. These may affect the quantitative results but at least the qualitative feature may remain unchanged because the Fermi surfaces of electrons and holes are quite small spheres. The existence of the Γ_8 band may be responsible for the lower temperature anomaly.[7]

In order to investigate the possibility of a magnetic transition and an anomalous magnetic field effect, the random phase approximation (RPA) is employed. Since RPA overestimates the transition temperature, we use the small value of the Coulomb interactions in this case, which is considered as the renormalized one in the low-energy regime in the rare-earth compounds. Furthermore, since the Coulomb interaction acts only on f electrons, ordered states will be mainly determined by the localized f electrons, so that only the f-f component of the correlation function is considered, for simplicity. It is essential for the following theory to calculate both the parallel and perpendicular elements to the external field of the static susceptibility, which are given by

$$\chi^x(\mathbf{q}) = \chi^y(\mathbf{q}) = \frac{\beta^2}{2}\frac{\chi^0_{\uparrow\downarrow}(\mathbf{q})}{1 - U\chi^0_{\uparrow\downarrow}(\mathbf{q})}, \tag{2}$$

$$\chi^z(\mathbf{q}) = \frac{\beta^2}{4}\frac{\chi^0_{\uparrow\uparrow}(\mathbf{q}) + \chi^0_{\downarrow\downarrow}(\mathbf{q}) + 2U\chi^0_{\uparrow\uparrow}(\mathbf{q})\chi^0_{\downarrow\downarrow}(\mathbf{q})}{1 - U^2\chi^0_{\uparrow\uparrow}(\mathbf{q})\chi^0_{\downarrow\downarrow}(\mathbf{q})} \tag{3}$$

where $\chi^0_{\sigma\sigma'}$ is the band susceptibility and is defined as

$$\chi^0_{\sigma\sigma'}(\mathbf{q}) = \frac{-T}{N}\sum_{\mathbf{k},\omega_n} g^{\rm f}_{\sigma}(\mathbf{k}+\mathbf{q}, {\rm i}\omega_n) g^{\rm f}_{\sigma'}(\mathbf{k}, {\rm i}\omega_n), \tag{4}$$

$$g^{\rm f}_{\sigma}(\mathbf{k}, {\rm i}\omega_n) = \frac{1}{{\rm i}\omega_n + \mu - \epsilon^f_{\mathbf{k}\sigma} - \dfrac{V^2}{{\rm i}\omega_n + \mu - \epsilon^c_{\mathbf{k}\sigma}}}. \tag{5}$$

T is the temperature and N is the number of sites. μ is the chemical potential and $\omega_n (= (2n+1)\pi T)$ represents the odd Matsubara frequency. $\epsilon^c_{\mathbf{k}\sigma}$ and $\epsilon^f_{\mathbf{k}\sigma}$ are the energy dispersion with the Zeeman terms. Note that we use the relation that $\chi_{\downarrow\uparrow}(\mathbf{q})$ is always equal to $\chi_{\uparrow\downarrow}(\mathbf{q})$ within the RPA to derive χ^x.

We numerically calculate the above-mentioned equations. The summations are efficiently carried out by using the fast Fourier transform with $N = 128 \times 128 \times 128$ points in the $\mathbf{k}$ summation and 4096 Matsubara frequencies in the ω_n summation. Note that the hopping amplitude α_c is taken to be unity for simplicity.

To discuss the instability to ordered states, the band susceptibility, $\chi^0(\mathbf{q}) \equiv \chi^0_{\uparrow\uparrow}(\mathbf{q}) = \chi^0_{\downarrow\downarrow}(\mathbf{q}) = \chi^0_{\uparrow\downarrow}(\mathbf{q})$ for $B_{\rm ext} = 0$, is shown in Fig. 2. The largest value appears at the H point $\mathbf{q} = (1, 0, 0)$ in units of $2\pi/a$. Since the Fermi surfaces of electrons and holes are quite small spheres, the peak of $\chi^0(\mathbf{q})$ appears at $\mathbf{q} = (1, 0, 0)$ at low temperatures, which corresponds to the difference between the top of the lower band (Γ point) and the bottom of the upper band (H point) in Fig. 1. Recently, the result of the neutron scattering for $CeOs_4Sb_{12}$ at $B_{\rm ext} = 0$ found that the nesting vector corresponds to $\mathbf{q} = (1, 0, 0)$.[13] Therefore, our obtained result of the susceptibilities is consistent with the experiment at $B_{\rm ext} = 0$.

The basic lattice structure of $CeOs_4Sb_{12}$ is BCC. For the single band Hubbard model at half-filling with only the nearest neighbor hopping, the perfect nesting at the wave vector $\mathbf{q} = (1, 0, 0)$ exists. In such a case, it is known that the infinitesimally small U causes the metal-SDW transition at $T = 0$. Although the perfect nesting is lost in the present model due to the hybridization and the next nearest neighbor hopping, the Fermi surfaces are

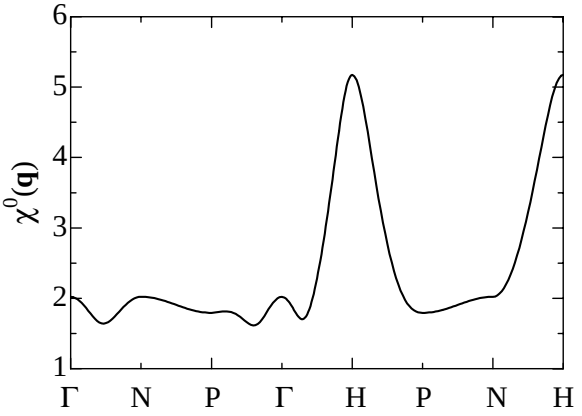

Fig. 2. Static irreducible susceptibility for various momenta in the absence of an external field at $T = 0.002$, where $\chi^0(\mathbf{q}) = \chi^0_{\uparrow\downarrow}(\mathbf{q}) = \chi^0_{\uparrow\uparrow}(\mathbf{q}) = \chi^0_{\downarrow\downarrow}(\mathbf{q})$.

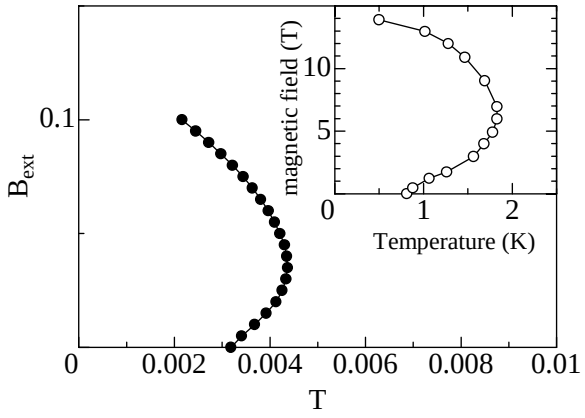

Fig. 4. The T-B Phase diagram of the metal-SDW transition at $U = 0.2$. The inset shows the experimental result obtained by Sugawara *et al.*[2)]

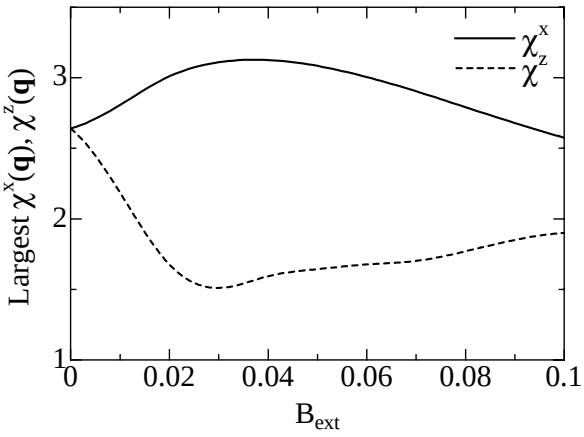

Fig. 3. The largest susceptibilities as a function of the magnetic field at $T = 0.002$ and $U = 0.0$. Solid (dashed) line represents $\chi^x(\mathbf{q})$ ($\chi^z(\mathbf{q})$).

in the vicinity of the nesting. Therefore, in the absence of an external field, the metal-SDW transition occurs at $U_c = 0.2$ at $T \sim 0.003$ within the RPA in the present model.

Next, let us discuss the effects due to the external magnetic field. The field dependence of the largest values of susceptibilities is shown in Fig. 3. With an increase in the magnetic field along the z direction, χ^x is first enhanced in small field region. As the external field is increased further, χ^x is suppressed. The vector $\mathbf{q}$, which gives the largest values of susceptibilities, does not change within $B_{\rm ext} < 0.2$. In contrast to the behavior of χ^x, χ^z is first suppressed. This behavior is reasonable since the spin-spin correlation functions along the external field are generally suppressed when the weak external field is applied. Furthermore, with a further increase in the external field, the maximum value of χ^z is enhanced. In this range of the field, the vector $\mathbf{q}$, which gives the largest values of the susceptibilities, is gradually changed. Both the susceptibilities are suppressed under a larger external field (not shown). These behaviors and mechanisms are similar to our previous theory for $CeRhIn_5$, where the more precise FLEX (fluctuation-exchange) method was used.[14)]

In general, the response functions are strongly affected by the form of the Fermi surface and the effective mass. However, since the Fermi surfaces of electrons and holes at $B_{\rm ext} = 0$ are quite small spherical pockets in the present model, the geometrical structures of each Fermi surface are not essential for our discussions. In addition, the sizes of both the Fermi surfaces remain the same even if their effective mass changes because the volumes in the $\mathbf{k}$-space are the same. Also, in the presence of a the weak external magnetic field, the change of the band structure may be small, so that the effective mass may not change the response functions qualitatively. The present band structure at $B_{\rm ext} = 0$ is close to the nesting, so that the change in magnetic susceptibilities by the external field becomes large. Therefore, it is possible that when the weak external field is applied, the nesting condition is rather improved because the spin bands are shifted by the field and approach the nesting condition.

These results indicate that the presence of the external field enhances the instability for the ordered states. In three-dimensional systems, ordered states can occur at a finite temperature. Namely, the anomalous metal-insulator transition may occur in the present model with an appropriate value of the Coulomb repulsion. Figure 4 shows the temperature-external field phase diagram of the metal-SDW transition. Note that the instability occurs not in $\chi^z(\mathbf{q} = (1, 0, 0))$ but in $\chi^x(\mathbf{q} = (1, 0, 0))$ (and χ^y), which indicates the appearance of a magnetic moment component perpendicular to the field. This can be verified in the future by an experiment. In the small external field region, the phase transition temperature $T_{\rm N}$ is enhanced with the increase in $B_{\rm ext}$ such that the slope of the phase boundary becomes positive. Thus, the anomalous phase transition observed in $CeOs_4Sb_{12}$ can be qualitatively reproduced.

It should be noted that in order to calculate magnetic susceptibilities, we employ the RPA, which is insufficient to take the effect of quantum fluctuations into account. Quantum fluctuations particularly become important in

the vicinity of quantum critical points where antiferromagnetic correlations are enhanced.[14] However, correlation effects are essential in the weak external field region. By taking quantum fluctuations into account, e.g., via the FLEX approximation,[14] the metal-SDW transition temperature is reduced and the transition boundary as a whole shifts to the low temperature region. In particular, the shift becomes conspicuous in the weak external field region. However, the overall structure of the phase boundary obtained here may not qualitatively change.

Furthermore, we comment on the multi-band effects of f orbitals. In our model, we neglect the degeneracy of f orbitals for simplicity. However, in the published band calculation, one of the bands comprised of the 4f Γ_8 states has a minimum at the Γ point, though slightly above E_F, which is neglected in our model. However, we consider that the nesting property between the top of the valence band at Γ and the bottom of the Γ_7 band at H is primary responsible for the SDW transition and anomalous phase diagram. Therefore, the qualitative properties of $CeOs_4Sb_{12}$ can be reproduced by using the present simple model.

The semimetallic band structure is employed in the present model by considering the experimental results. However, when a Kondo-insulator-like band structure with a rather small hybridization gap is employed, the anomalous transition can be observed more clearly. When the hybridization gap vanishes due to the Zeeman splitting, the nesting condition of the Fermi surfaces is conspicuously improved, where the response function is enhanced.[15] A similar anomalous magnetic field effect is also investigated for the Kondo insulator.[16,17] In this case, the ordered phase appears in a finite field since the element of the spin-spin correlations perpendicular to the external field is enhanced.

In summary, we have investigated the anomalous phase transition observed in $CeOs_4Sb_{12}$. By constructing the effective tight-binding model with the Coulomb interaction between f electrons, whose band structure is in the vicinity of the nesting, the metal-SDW phase boundary is determined within the mean field approximation. The nesting condition of the Fermi surfaces is improved when the weak external field is applied such that the slope of metal-SDW phase boundary becomes positive and the anomalous transition can be reproduced. This anomalous transition occurs when the top of the lower band (Γ point) and the bottom of the upper band (H point) are located close to the Fermi level. A small moment perpendicular to the applied magnetic field should be induced,[18] which can be verified in a future experiment.

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18) Although the spin-structure is not yet clarified in the experiment, some magnetic anisotropy determining the direction of the moments might exist. In that case, the divergence of $\chi^{x,y}$ at $B > 0$ might yield only a small canting of the moments from the easy axis. Otherwise, an application of B suddenly changes the direction of the moments.