Two-state Weiss model for the anomalous thermal expansion in EuNi$_2$P$_2$

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Abstract

It has recently been found that the single crystalline EuNi$_2$P$_2$ shows an anomalous thermal expansion and its scaling relation to the average 4$f$ electron number. We point out that a phenomenological 2-state Weiss model can explain these behaviors. We also show that the model leads to the observed effective Bohr magneton number per atom (7.4 $\mu_B$) in the high-temperature limit, and is consistent with the temperature dependence of experimental susceptibility. Moreover the model predicts that the 4$f$ contribution to the thermal expansion coefficient is in proportional to that of the specific heat. The results suggest that the strong temperature dependence found in these experimental data originates in the excitations from the heavy-fermion ground state to the independent 4$f^7$ atomic states.

Keywords: Thermal expansion, Weiss model, 2$\gamma$-state model, EuNi$_2$P$_2$, Valence fluctuations, Heavy-fermions

1. Introduction

Europium compounds are known to show a variety of magnetic and thermal properties due to existence of different valence states $[1, 2, 3, 4, 5]$. In the divalent compounds, Eu ions have 4$f^7$ configuration (Eu$^{2+}$) with atomic spin $S = 7/2$, angular momentum $L = 0$, and total angular momentum $J = 7$.
$J = 7/2$ showing a large magnetic moment, while in the trivalent compounds, Eu ions have $4f^6$ configuration (Eu$^{3+}$) with $S = L = 3$, and $J = 0$, thus no magnetic moment. Some of these compounds such as EuPd$_2$Si$_2$ [6], EuNi$_2$(Si$_{0.18}$Ge$_{0.82}$)$_2$ [7], and EuRh$_2$Si$_2$ [8] show the valence instability with increasing temperature, pressure, and magnetic field. In particular, EuNi$_2$P$_2$ has recently received much attention because it shows both heavy-fermion and mixed-valence behaviors. In fact, M"ossbauer isomer-shift experiment reports a mixed valence state even at zero temperature [9] and the electronic specific heat coefficient $\gamma$ shows a large value of 100 mJ/(K$^2$·mol) [10].

Quite recently, Hiranaka et. al. [11] grew the single crystalline EuNi$_2$P$_2$ and carried out systematic measurements of resistivity, specific heat, susceptibility, and thermal expansion. The low-temperature data of resistivity and specific heat show the heavy-fermion behavior with a large electronic specific heat coefficient $\gamma = 93$ mJ/(K$^2$·mol). The susceptibility data show the Curie-Weiss behavior with the effective Bohr magneton number $p_{\text{eff}} = 7.4 \mu_B$/Eu and the Weiss constant $\Theta = -120$ K in the high temperature regime, and becomes almost constant ($\approx 0.04$ emu/mol) below 50 K. Anomalous $4f$ electronic contribution to the volume expansion $(\Delta V/V)_{4f}$ is found to increase rapidly up to 100 K and tends to saturate with increasing temperature. The new aspect which they found is that the temperature variation of $(\Delta V/V)_{4f}$ scales well to that of the average Eu valence. Because the present system shows both the heavy-fermion and mixed-valence behaviors and the anomalous volume expansion continues up to 200 K, which is far above the experimentally suggested Kondo temperature $T_K$ ($\sim 80$ K), the scaling relation may be controlled by an extra-parameter other than $T_K$, i.e., a valence fluctuation temperature $T_v$.

In this paper, we point out that the temperature dependence of volume thermal expansion and its scaling relation to the average $4f$ electron number found in experiment are basically explained by a simple and phenomenological $2\gamma$-state model. The model was first proposed by Weiss [12] to explain the anomalous thermal expansion of $\gamma$Fe and the Fe-Ni Invar alloys [13]. It assumes the existence of two magnetic states, a low-spin small-volume state and a high-spin large-volume state. The former is assumed to be the ground state in $\gamma$Fe, while the latter is assumed to be stabilized at the ground state in the Invar alloys [13, 14, 15]. One can describe the excitations from the ground state to the independent excitations on sites with use of the Weiss model even in the itinerant electron system.

We remark that apart from the anomalous volume expansion, the Weiss
model is somewhat similar to the interconfiguration fluctuation (ICF) model for some rare-earth compounds \[9, 16, 17, 18, 19\]. The present model however differs from the ICF model in the following points. (1) The Weiss model assumes the nondegenerate metallic ground state (\(i.e.,\) a heavy-fermion state in the present case), while the ICF model assumes the 4f atomic state with an integral 4f electron number as the ground state. (2) The Weiss model does not make use of any other assumptions, while the ICF model introduces phenomenologically a fluctuation temperature \((T_{sf})\) corresponding to the width of the 4f level state.

In the following section, we apply the concept of the 2\(\gamma\)-state model in order to explain a strong temperature dependence which is seen in the experimental data of EuNi\(_2\)P\(_2\). With use of the 2-state Weiss model, we will demonstrate that the model explains an overall temperature dependence of thermal expansion, its scaling relation to the 4\(f\) electron number, the specific heat, and the susceptibility. We summarize the conclusion in the last section 3.

2. Two-state Weiss model for EuNi\(_2\)P\(_2\)

2.1. Thermal expansion and scaling relation

Experimentally, a heavy-fermion state is realized in EuNi\(_2\)P\(_2\) at low temperatures. We therefore assume that the ground state is a nonmagnetic heavy-fermion state with a small volume per atom \(V_L\) as found experimentally, and call this state ‘the low spin state’ hereafter. We neglect the low energy excitations associated with the heavy-fermions which yields the \(T\)-linear specific heat. Instead, we take into account independent excitations to the atomic Eu\(^{2+}\) state with \(J = J_H (= 7/2)\) and a large volume \(V_H\). We call the single-site excited state on each site ‘the high spin state’. The volume per Eu atom is then characterized by \(J\) as \(V(J)\), and the thermal average \(V\) is given by

\[
V = \frac{\sum J \sum_{M=-J}^{J} V(J) e^{-\beta E_J}}{\sum J \sum_{M=-J}^{J} e^{-\beta E_J}}.
\]

Here \(\beta\) is the inverse temperature and \(E_J\) denotes the energy of the system with the state \(J\). Note that we allocated \(‘J = 0’\) to ‘the low-spin state’
Figure 1: Temperature dependence of 4f electron contribution to the thermal expansion ($\Delta V/V$). Closed circles: Experimental results [1], solid line: result of 2-state Weiss model for $\Delta E/k_B = 150$ K.

For convenience. It does not mean that the ground state is Eu$^{3+}$ ($J = 0$). Instead, $E_{J=0}$ is defined by the ground state energy per Eu atom $E_L$ and $V(J = 0) \equiv V_L$. Similarly, $E_{J_H} = E_H$ denotes the excitation energy per atom in the high-spin state and $V(J = J_H) \equiv V_H$.

After simple calculations of the r.h.s. of Eq. (1), we obtain the following expression for volume.

$$V = V_L + v_0 \frac{w e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}.$$  \hspace{1cm} (2)

Here $v_0 = V_H - V_L$, $w = 2J_H + 1 (= 8)$, and $\Delta E = E_H - E_L$ is the excitation energy from the low-spin state (L) to the high-spin state (H). $T_v \equiv \Delta E/k_B$ is interpreted as a valence fluctuation temperature in the present system. The thermal expansion $\Delta V/V_L = (V - V_L)/V_L$ is therefore given by

$$\frac{\Delta V}{V_L} = \frac{\Delta V(\infty)}{V_L} \frac{(1 + w) e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}.$$  \hspace{1cm} (3)

Here $\Delta V(\infty)/V_L$ denotes the volume change in the high-temperature limit.
Figure 2: Specific heat in the present model (solid curve) and experimental data (closed circles)\textsuperscript{[11]}. Thin solid curve shows the electronic contribution $C_{\text{v}}^{(e)}$, which is calculated from Eq. (9) with use of the same parameter $\Delta E/k_B = 150$ K as in Fig. 1. Dashed curve is the lattice contribution calculated by the Debye model. The Dulong-Petit parameter $A$ and the Debye temperature parameter $T_D$ are chosen to be $A = 15.9$ in unit of the gas constant and $T_D = 350$ K so that the experimental data around 50 K and 200 K are reproduced.

Figure 1 shows a numerical result of $\Delta V/V_L$ compared with the experimental data. We adopted the experimental value $\Delta V(\infty)/V_L = 7.3 \times 10^{-3}$ at 300 K\textsuperscript{[11]} in the calculations. With use of a characteristic temperature $T_v = \Delta E/k_B = 150$ K, we find that the formula (3) explains the overall feature of the experimental thermal expansion. The deviation from the data at low temperatures is attributed to the fact that the model does not take into account the low-energy excitations associated with the heavy-fermion states.

We obtain in the same way the average $4f$ electron number as

$$n_f = n_{fL} + n_0 \frac{w e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}.$$

(4)

Here $n_0 = n_{fH} - n_{fL}$, $n_{fL}$ ($n_{fH}$) being the electron number in the low-spin (high-spin) state. Note that $n_{fL}$ is the average $f$ electron number per Eu
atom in the heavy-fermion ground state (i.e., \( n_f L \neq 6 \)). Equation (4) implies that there is a scaling relation between the volume change \( \Delta V / V_L \) and that of \( 4f \) electron number \( \Delta n_f = n_f - n_{fL} \):

\[
\frac{\Delta V}{V_L} = \frac{v_0}{n_0 V_L} \Delta n_f.
\] (5)

The relation is in agreement with the experimental fact [11]. According to the Mössbauer experiment, \( n_f(T = 0) \sim 6.5 \) and \( n_f(T = \infty) \sim 6.75 \) [9]. Using Eq. (5) and these values, we obtain \( n_{fH} \sim 6.8 \), which is rather close to the atomic value 7.0.

2.2. Specific heat

Similar scaling relation is found between the electronic contribution to the volume thermal expansion coefficient \( \alpha^{(e)}_v = V_L^{-1} \partial V / \partial T \) and that to the heat capacity \( C^{(e)}_v \). In fact, the internal energy \( E \) in the Weiss model is given by

\[
E = E_L + \Delta E \frac{w e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}.
\] (6)

Thus we have a relation,

\[
E - E_L = \Delta E \frac{V_L \Delta V}{v_0 V_L},
\] (7)

and find a scaling relation,

\[
\alpha^{(e)}_v = \frac{1}{\Delta E V_L} \frac{v_0}{V_L} C^{(e)}_v.
\] (8)

Here \( C^{(e)}_v \) is the electronic contribution in the present model, being given by

\[
C^{(e)}_v = \frac{w (\beta \Delta E)^2 e^{-\beta \Delta E}}{(1 + w e^{-\beta \Delta E})^2}.
\] (9)

It should be noted however that the relation (8) does not necessarily mean that the Schottky-like anomaly is visible in the experimental data of specific heat \( C_v \), though the data of the volume expansion coefficient show a clear anomaly around 40 K [11]. In order to see this point, we consider here a simple Debye model as a lattice contribution \( C^{(l)}_v \) to the specific heat:
\( C_v^{(l)} = AD(T_D/T) \). Here \( A(\sim 15) \) is the Dulong-Petit constant, \( T_D \) is the Debye temperature and \( D(x) \) is the Debye function. The total specific heat is given by \( C_v = C_v^{(e)} + C_v^{(l)} \). Figure 2 shows the calculated specific heat vs experimental data. The present theory is consistent with the experimental data of the specific heat, and we find that the anomalous contribution cannot be seen in the total \( C_v \) because of a large lattice contribution of \( C_v^{(l)} \) and its steep slope in the temperature region between 40 K and 80 K [20].

2.3. Susceptibility

The susceptibility in the 2-state Weiss model is obtained by adding the Zeeman term to the Hamiltonian. The magnetization \( \langle M_z \rangle \) per Eu atom under the magnetic field \( H \) is calculated from the following expression.

\[
\langle M_z \rangle = \sum_{JM} (M_z)_{JM} e^{-\beta E_{JM}} = \frac{\sum_{JM} (M_z)_{JM} e^{-\beta E_{JM}}}{\sum_{JM} e^{-\beta E_{JM}}}. \tag{10}
\]

Here the ‘\( J = 0 \)’ state is the heavy-fermion ground state under the magnetic field \( H \). With use of the energy \( E_L \) and the heavy-fermion ground-state susceptibility \( \chi_L \) which might be inversely proportional to the Kondo temperature, the energy under the magnetic field should be given by

\[
E_{JM} = E_L - \frac{1}{2} \chi_L H^2. \tag{11}
\]

The magnetization per atom in the low spin state is therefore given by

\[
(M_z)_{JM} = -\partial E_{JM}/\partial H = \chi_L H. \tag{12}
\]

On the other hand, the energy in the high spin state (\( J = J_H \)) is given by

\[
E_{JM} = E_J - g_J M H - \frac{1}{2} \alpha_{JM} H^2. \tag{12}
\]

Here \( g_J \) is Landé’s \( g \) factor, \( \alpha_{JM} \) is a phenomenological Van Vleck constant [5, 21]. The magnetization is given by

\[
(M_z)_{JM} = -\partial E_{JM}/\partial H = g_J M + \alpha_{JM} H. \tag{12}
\]

From Eqs. (11), (11), and (12), we obtain the susceptibility.

\[
\chi = \chi_L + \left( \Delta \chi + \frac{P_H^2}{3k_BT} \right) \frac{w e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}. \tag{13}
\]
Figure 3: Temperature dependence of susceptibilities ($\chi$). Open circles: experimental data [11] for $H//[110]$, closed circles: experimental data [11] for $H//[001]$, solid line: present result based on the 2-state Weiss model for $\chi_L \approx 0.037$ emu/mol, $\Delta \chi = -0.044$ emu/mol, $\Theta = -120$ K, and $\Delta E/k_B = 150$ K (see Eq. (15)).

Here $\Delta \chi = \chi_H - \chi_L$, and $\chi_H$ is the susceptibility at $T = 0$ in the high-spin state defined by $\sum_M \alpha_{J_H M} / (2J_H + 1)$. $p_H$ is the effective Bohr magneton number in the high-spin state, i.e., $p_H^2 = g_J^2 J_H (J_H + 1)$. Taking the high-temperature limit, we obtain the effective Bohr magneton number $p_{\text{eff}}$ as

$$p_{\text{eff}} = \sqrt{\frac{w}{1 + w} p_H}.$$  \hspace{1cm} (14)

Using the values $w = 8$ and $p_H = \sqrt{63}$, we obtain $p_{\text{eff}} = 7.48 \mu_B$, which is in good agreement with the experimental value 7.4 $\mu_B$ [11].

The susceptibility [13] however does not explain an overall temperature variation of the experimental data. We have to take into account the effect of polarization due to the RKKY-like magnetic interaction via conduction electrons. This produces an effective magnetic field according to the mean-field picture and should produce the Weiss constant $\Theta$ in the susceptibility.
when \( J = J_H \). We reach then the following susceptibility.

\[
\chi = \chi_L + \left( \Delta \chi + \frac{C_H}{T - \Theta} \right) \frac{w e^{-\beta \Delta E}}{1 + w e^{-\beta \Delta E}}.
\]  

(15)

Here \( C_H = p_H^2/3k_B \) is the Curie constant in the high-spin state. It should be noted that the polarization effects due to the magnetic field are negligible for the other quantities because they are of order of \( H^2 \).

Using the experimental values \( \Theta = -120 \) K and \( \chi_L \approx 0.037 \) emu/mol \[11\] and choosing \( \Delta \chi \) as \( \Delta \chi = -0.044 \) emu/mol, we can explain the global feature of temperature dependence of EuNi\(_2\)P\(_2\) as shown in Fig. 3. Note that we did not take into account the anisotropy due to tetragonal structure in the present analysis for simplicity.

3. Summary

We have shown in this paper that the phenomenological 2-state Weiss model with an emphasis of local excitations explains an overall feature of the volume expansion due to 4\( f \) electrons as well as the scaling relation between the 4\( f \) electron contribution to the volume expansion and the average 4\( f \) electron number. These results indicate that the strong temperature dependence of thermal expansion found in this system is mainly determined by local excitations associated with valence fluctuations. We also predicted that there is another scaling relation between the thermal expansion coefficient due to the 4\( f \) electrons and the associated specific heat. We have also shown that calculated effective Bohr magneton number in the high-temperature limit is in good agreement with the experimental value 7.4 \( \mu_B \)/Eu. For explanation of temperature dependence of susceptibility, we need inter-site magnetic interactions via conduction electrons. Modified susceptibility explains the temperature dependence of the experimental data, and indicates that there are three temperature scales, the characteristic temperature \( T_v = \Delta E/k_B \) (\( \sim 150K \)) for on-site valence fluctuations, the Weiss constant \( \Theta \) (\( \sim -120K \)) associated with the RKKY type interactions via conduction electrons, and the Kondo temperature \( T_K \) for the formation of heavy-fermions. The results presented in this paper indicate that the heavy-fermion ground state is collapsed by valence fluctuations which are characterized by \( T_v \). In this sense, the characteristic temperature \( T_v \) plays an essential role in the physics of EuNi\(_2\)P\(_2\). It has not yet been clarified theoretically whether or not the Kondo temperature is well-defined in this system.
Although the present model is consistent with the heavy-fermion ground state as well as the effective Bohr magneton number in the high temperature limit which is directly related to the local excitations of $4f^7$, it does not take into account the low energy excitations. The temperature dependence associated with the heavy-fermions is not described here. The deviation of $\Delta V/V$ from the experimental data below 40 K in Fig. 1 should be attributed to this fact. Too small a specific heat below 30 K found in Fig. 2 is due to the neglect of the low energy excitations. Microscopic derivation of the phenomenological model and the inclusion of the low-energy excitations are left for future investigations.

The present work is supported by a Grant-in-Aid for Scientific Research (25400404).

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