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RESEARCH ARTICLE

Unusual crystal-lattice behaviour of CeSb at ambient pressure

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Abstract: The temperature dependence of lattice constant of CeSb in the temperature range from 17 K to 280 K as measured by the X-ray diffraction technique exhibits an unusual minimum around 45 K. The origin of this exotic lattice behaviour has been disclosed in this article. Our model analysis shows that two types of Ce ions with different sizes, called Γ_7 and Γ_8 Ce ions, appear in the CeSb lattice in its paramagnetic phase to exhibit its unusual temperature dependence of lattice constant. The calculated lattice constant difference $a_7(0)$- $a_8(0)$ at 0 K between a CeSb lattice with pure Γ_7 Ce ions and a CeSb lattice with pure Γ_8 Ce ions is 0.0081 Å, which is very small. The lattice contraction δ, defined by $\delta = \{a_7(0) - a_8(0)\}/a_7(0)$ in the present analysis, is 1.263×10^{-3}.

Keywords: Cerium monopnictides, CeSb, low carrier-density, *p-f* mixing, X-ray diffraction.

INTRODUCTION

Cerium monopnictides Ce*X* (*X*=P, As, Sb and Bi) with the NaCl-type crystal structures are compensated semi-metals. They have extremely low carrier-density, about 0.01, 0.005, 0.04 and 0.06/Ce for CeP, CeAs, CeSb and CeBi, respectively at low temperature[1-3]. They exhibit unusual transport and magnetic properties. The single electron in the 4*f* orbital of Ce^{3+} ion is responsible for the magnetic properties of these materials. By Hund's rule, J =5/2 state is the ground state (Figure 1) of Ce^{3+} ion because it stays in a state with S=1/2 and L=3. The excited J=7/2 state lies at 0.28 eV (~3250K) above the ground state[4]. Due to the crystal field effect, the ground-state J=5/2 multiplet splits into a Γ_7 doublet and a Γ_8 quartet with Γ_7 as the ground state[4-6]. Inelastic neutron experiments revealed the values of crystal-field splittings (E) at about 160, 150, 37 and 8 K for CeP, CeAs, CeSb and CeBi, respectively at low temperatures[4-6].

The present work is concerned with CeSb. This compound is well-known with its complicated phase diagram in the magnetic field (H) - temperature (T) plane with 14 different magnetic phases[7-10]. Their magnetic structures are formed with various sequences of ferromagnetic (0 0 1) planes of almost fully polarized Γ_8-like Ce ions (moment value ~2 μ_B). Paramagnetic Γ_7 Ce-ion planes are also found to exist in some of these structures.

The motivation for the present work of the measurement of temperature variation of lattice constant came from the reported results of temperature-dependent lattice constants of CeP and CeAs[11]. The reported results were obtained from the single crystal X-ray diffraction experiments on these compounds in a wide temperature range. The lattice constants of CeP and CeAs exhibit minima at 120 K and 90 K, respectively[11]. Large lattice contractions with increasing temperatures are observed above their Néel temperatures, T_N . Their values at T_N become as same as those at 250 K and 200 K, respectively. The sample in the present work, CeSb, exhibits a minimum at 45 K in the temperature-dependent lattice constant measured in the temperature range from 6 − 280 K (Figure 3). In this case the lattice constant at T_N becomes the same as that of at 120 K. The previous report showed the tetragonal structural phase transition of CeSb below T_N = 16 K[12]. The tetragonal structural phase transition due to magnetic ordering is found to be below T_N = 17 K in the present work.

In this study, we observed an unusual temperature dependence of lattice constant in the temperature range from 17 − 280 K of CeSb at ambient pressure. This unusual behaviour of the lattice constant has been explained by introducing a model as mentioned in the analysis.

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METHODS AND MATERIALS

X-ray diffraction technique was employed for the measurement of lattice constant of CeSb with temperature variation from 6 − 280 K. The conventional X-ray source, with a rotating anode of Molybdenum (Mo) (Neutron Scattering Lab., Tokyo Metropolitan University, Japan) was used in the experiment. The sample of CeSb with the size of 2.6×2.4×0.9 mm^3 was cleaved from a large single crystal which was used in the previous X-ray study on the superlattice formations[13]. The sample with a cleaned flat surface of the (0 0 1) plane was mounted in a closed-cycle refrigerator, and it was installed on the X-ray spectrometer. The experimental set-up is illustrated in Figure 2. A monochromator and an analyzer of pyrolytic graphite crystals were adopted to select only the K_α X-ray [$\lambda(K_{\alpha1}) = 0.709$Å, $\lambda(K_{\alpha2}) = 0.713$Å] and to reduce the background counts.

The experimental data of lattice constant in the temperature range from 17 − 280 K has been fitted by the least-squares fitting method and IGOR Pro software[14].

The heat capacity C_V of a solid, according to the Debye approximation is given by

$$C_V = 9N\,k_B\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} \frac{x^4 \exp(x)}{(\exp(x)-1)^2}\,dx \qquad \text{.....(1)}$$

Here, N is the number of primitive cells in the specimen,

$$x = \frac{\hbar\omega}{k_B T} \quad \text{and} \quad x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T}$$

The coefficient of volume expansion α of a solid is defined as the ratio of the increase in volume of the solid per degree rise of temperature to its original volume. Mathematically α is expressed as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N} \qquad \text{..... (2)}$$

at constant pressure, P and at constant density of ions, N.

On the basis of oscillator model of the solid, Grüneisen predicted that the three important physical properties of a solid − the coefficient of volume expansion α, the specific heat at constant volume C_V, and the compressibility K − are linked together through the relation[15].

$$\alpha = \gamma \frac{K}{V} C_V \qquad \text{..... (3)}$$

where γ , a constant independent of temperature, is called the Grüneisen constant. V in Equation (2) is the volume of the solid under consideration. The Grüneisen constant (parameter) γ is defined as

$\gamma = -\frac{V}{\theta_D}\frac{\partial \theta_D}{\partial V} = -\frac{\partial \ln \theta_D}{\partial \ln V}$ and the compressibility K is defined as $K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. We find from Equation (3) that α is proportional to the specific heat C_V at all temperatures, and thus α and C_V should have the same temperature dependence.

From Equation (2) we can write,

$$\frac{\Delta V(T)}{V(T)} = \alpha \Delta T$$

or, $\frac{\Delta a^3(T)}{a^3(T)} = \alpha\ \Delta T$

or, $\frac{\Delta a(T)}{a(T)} = \frac{1}{3}\alpha\ \Delta T$ ..... (4)

We have $a\ (T) = \alpha\ (0)$ at $T = 0$ K, hence we can write Equation (4) in the following way

$$\frac{1}{a(0)}\left[a(T) - a(0)\right] = \int_0^T \frac{1}{3}\alpha(T')\,dT'$$

or, $a(T) = a(0) + \frac{a(0)}{3}\int_0^T \frac{\gamma K C_V}{V} dT'$ [Using Equation (3)]

or, $a(T) = a(0) + \frac{a(0)\gamma K}{3V}\int_0^T \{9Nk_B\left(\frac{T'}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x-1)^2}\} dT'$

[Using Equation (1)]

or, $a(T) = a(0) + \frac{a(0)}{3}\left(\frac{\gamma K}{V} 9Nk_B\right)\left[\left(\frac{\theta_D}{T}\int_0^{\frac{\theta_D}{T}} dx \frac{x^4 e^x}{(e^x-1)^2}\right)\right.$

$$\left.\int_0^T \left(\frac{T'}{\theta_D}\right)^3 dT' - \int_0^T \left\{\frac{d}{dT'}\left(\frac{\theta_D}{T}\int_0^{\frac{\theta_D}{T}} dx \frac{x^4 e^x}{(e^x-1)^2}\right)\int_0^T \left(\frac{T'}{\theta_D}\right)^3 dT'\right\} dT'\right]$$

or,

$$a(T) = a(0) + \frac{a(0)}{3}\left(\gamma \frac{K}{V} 9Nk_B\right)$$

$$\left[\frac{T^4}{4\theta_D^3}\int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x-1)^2}dx + \int_0^T \frac{\theta_D^2}{4T'^2}\frac{1}{\left(e^{\frac{\theta_D}{2T'}} - e^{-\frac{\theta_D}{2T'}}\right)}dT'\right] \quad \ldots (5)$$

In Figure 3 the open circles represent the observed temperature dependence of lattice constants of CeSb at ambient pressure. Tetragonal structural phase transition of the cubic lattice (*fcc*) is observed below T_N = 17 K. We are interested here in the temperature range from 17 − 280 K because there is an unusual lattice constant minimum around 45 K. This type of minimum cannot be explained by the Debye approximation of the temperature-dependent lattice constant $a(T)$ as given by Equation (5).

In order to explain the unusual temperature dependence of the lattice constant of CeSb in the paramagnetic phase (above 17 K), we assume that the interatomic bond length between cerium ions of Γ_8 state and pnictogens is shorter than that with Γ_7 cerium ions. This idea is schematically shown in Figure 4.

The energy of crystal field splitting between the Γ_7 ground state and the excited Γ_8 one is represented as E. The lattice constant of crystal composed of only cerium ions of Γ_7 state and pnictogen ones is expressed as $a_7(T)$, and that of only Γ_8 cerium ions is $a_8(T)$ which is expected to be shorter than $a_7(T)$. Then the fitting function of the observed lattice constant can be expressed as,

$$a(T) = \frac{2a_7(T) + 4a_8(T)e^{-E/k_B T}}{2 + 4e^{-E/k_B T}}$$

or,
$$a(T) = \frac{a_7(T)\left(2 + 4\frac{a_8(T)}{a_7(T)}e^{-E/k_B T}\right)}{2 + 4e^{-E/k_B T}} \quad \ldots\ldots\ldots (6)$$

Both of the terms, $a_7(T)$ and $a_8(T)$, are assumed to obey Equation (5). Their values at T= 0 K, $a_7(0)$ and $a_8(0)$, are left as fitting parameters. The energy of crystal field splitting is fixed to be E= 37 K for CeSb as mentioned in the introduction.

The optical phonon energy relevant to the Debye temperature is proportional to the factor of reduced mass[16],

$$\sqrt{\{(m_1+m_2)/m_1m_2\}}$$

where m_1 and m_2 are the masses of the rare earth ion and pnictogen one, respectively. But the optical phonon energy at Debye temperature is proportional to the Debye temperature. So the Debye temperature, θ_D is proportional to $\sqrt{\{(m_1+m_2)/m_1m_2\}}$. The Debye temperature of CeSb should be known in order to calculate $a(T)$ according to Equation (6). The reported

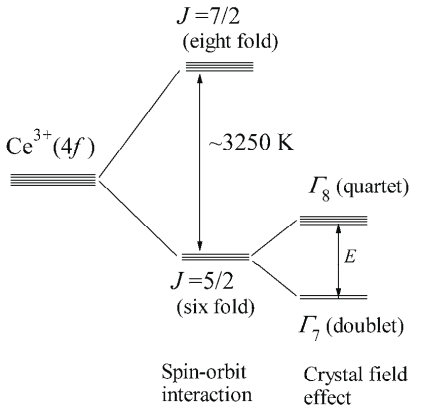

Figure 1: Schematic energy level splittings of 4f electron in Ce^{3+}ion.

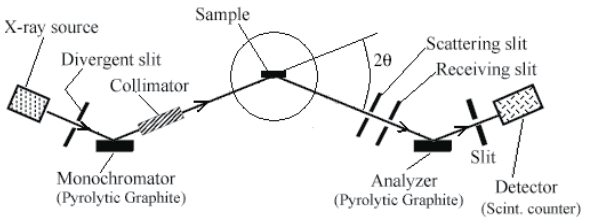

Figure 2: Schematic representation of the experimental set-up.

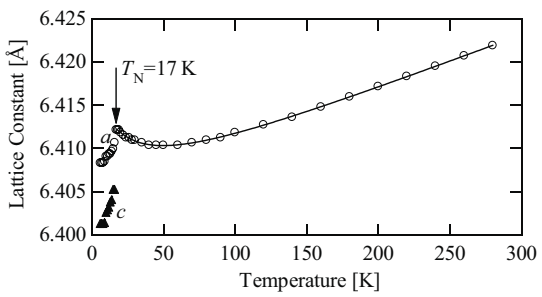

Figure 3: Temperature dependence of lattice constants of CeSb at ambient pressure

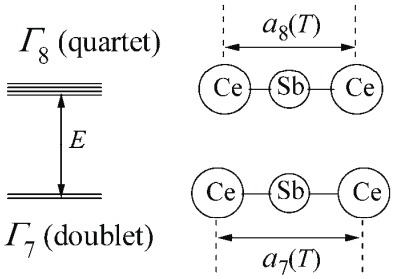

Figure 4: Schematic representation of crystal field levels and corresponding lattice parameters $a_7(T)$ and $a_8(T)$.

value of the Debye temperature of CeAs, θ_D(CeAs) is 242.5 K[11]. Using the above information the Debye temperature of CeSb, θ_D(CeSb) could be calculated in the following way.

$$\theta_D(\text{CeSb}) \propto \sqrt{(m_{Ce}+m_{Sb})/(m_{Ce}m_{Sb})} \quad \text{.....(7)}$$

and

$$\theta_D(\text{CeAs}) \propto \sqrt{(m_{Ce}+m_{As})/(m_{Ce}m_{As})} \quad \text{..... (8)}$$

Dividing Equation (7) by Equation (8) we get

$$\frac{\theta_D(\text{CeSb})}{\theta_D(\text{CeAs})} = \frac{\sqrt{(m_{Ce}+m_{Sb})/m_{Ce}m_{Sb}}}{\sqrt{(m_{Ce}+m_{As})/m_{Ce}m_{As}}}$$

or, $$\theta_D(\text{CeSb}) = \theta_D(\text{CeAs})\sqrt{\frac{(m_{Ce}+m_{Sb})m_{As}}{(m_{Ce}+m_{As})m_{Sb}}}$$

or, $$\theta_D(\text{CeSb}) = (242.5\text{K})\sqrt{\frac{(140+122)75}{(140+75)122}} = 209.9\text{K}$$

The value θ_D (CeSb) is needed in order to fit the temperature-dependent lattice constant of CeSb in the temperature range from 17 − 280 K.

We have fitted the experimental data in the temperature range 17 −280 K of Figure 3 by the Equation (6) with the least-squares fitting method and IGOR Pro software [14]. The fitting parameters at T=0 K are $w[0] = a_7(0)$,

$$w[1] = \gamma\frac{K_0}{V_0}Nk_B \quad \text{and} \quad w[2] = \frac{a_8(0)}{a_7(0)}.$$

The fitted values of the parameters with the errors are w[0] = (6.41375±5.4×10^{-5}) Å, w[1] = (6.36525×10^{-5} ± 3.14 ×10^{-7}) K^{-1} and w[2]=(0.998737±2.1×10^{-5}).

Hence we can write

$$\frac{a_8(0)}{a_7(0)} = 0.998737$$

or,

$$a_8(0) = (0.998737)\,a_7(0) = (0.998737)(6.41375\,\text{Å}) = 6.40565\,\text{Å}$$

Therefore, $a_7(0) - a_8(0) = 0.0081\text{Å}$

Thus the lattice constant difference [a_7(0)- a_8(0)] at 0 K between a CeSb lattice with pure Γ_7 Ce ions and a CeSb lattice with pure Γ_8 Ce ions is 0.0081 Å, which is very small.

RESULTS

Figure 3 shows the temperature dependence of lattice constant of CeSb at ambient pressure. From the fitting of the observed data in the temperature range from 17 − 280 K by the fitting function of Equation (6) and applying the least-squares fitting method we get $a_8(0)/a_7(0)$ = 0.998737 and $a_7(0)$ =6.41375 Å for CeSb. The fitted result is shown in Figure 3 by a solid line. The fitted curve reproduces the measured temperature dependence of the lattice constant well. The above results show that the lattice constant difference [$a_7(0) - a_8(0)$] between a CeSb lattice with pure Γ_7 Ce ions and a CeSb lattice with pure Γ_8 Ce ions is 0.0081 Å, a small difference we were able to detect by our analysis. The role of two types of Ce ions (Γ_8 Ce ion and Γ_7 Ce ion) was realized in the crystal-lattice by the model analysis in order to reproduce the observed lattice constant perfectly.

DISCUSSION

The crystal-lattice shrinking in Figure 3 above T_N is attributed to the increase of population of thermally excited Γ_8 state with smaller effective ionic size. Moreover, the crystal lattice shrinks suddenly below T_N and tetragonal distortion was observed. This phenomenon is also due to a smaller ionic size of the ordered Γ_8-like Ce ions and anisotropic 4*f*-electron orbital extending within the ferromagnetic *c*-plane due to strong *p-f* mixing effect. The value of lattice contraction δ, defined by $\delta = \{a_7(0) - a_8(0)\}/a_7(0)$, in our current analysis is 1.263×10^{-3}. The value of δ for CeSb found from the previous superlattice studies[17] of the magnetically ordered AFP3 phase at 14.7 K was 1.656×10^{-3}. The difference between these two values of δ is about 30%. This difference may arise from two facts:

(i) the present value of δ comes from the analysis of the temperature-dependent lattice constant data in the paramagnetic phase of CeSb, whereas its previous value comes from the magnetically ordered AFP3 phase, (ii) these two values of δ come from different measurement techniques and analyses.

The Debye temperature of any solid depends on the lattice parameter of the solid[18] or on the masses of the constituent atoms according to the form of Equation (7). The effect of carrier density on the Debye temperature may be an interesting topic. But, in Ce*X* (*X*= P, As, Sb and Bi), the carrier density and lattice parameter change simultaneously with *X*. Therefore it is difficult to see the effect of carrier density alone on the Debye temperature.

CONCLUSION

This model analysis shows that two types of Ce ions appear in the CeSb in its paramagnetic phase in order to exhibit the unusual temperature dependence of the lattice constant. The calculated lattice constant difference $[a_7(0)- a_8(0)]$ at 0 K between a CeSb lattice with pure Γ_7 Ce ions and a CeSb lattice with pure Γ_8 Ce ions is 0.0081 Å, which is very small. From the model analysis we could detect the simultaneous presence of two types of Ce ions, the Γ_7 and Γ_8 in the CeSb crystal. The lattice contraction δ in the present analysis is 1.263×10^{-3}, which is close to the reference value of 1.656×10^{-3}.

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The experimental part of this work has been performed using the X-ray spectrometer of the Neutron Scattering Laboratory, Department of Physics, Tokyo Metropolitan University (TMU), Japan. All concerned staff of TMU are cordially thanked for their kind cooperation and support during the experiment.

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