Anisotropic, thermal, and magnetic properties of CeAgSb$_2$: Explanation via a crystalline electric field scheme

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We have studied the thermal and magnetic properties of a single crystal of CeAgSb$_2$, which has a small net magnetic moment of about $0.4\mu_B$ below the ordering temperature $T_{ord}=9.7$ K, by means of specific heat, thermal expansion, and magnetization measurements. The magnetic part of the specific heat shows a broad peak around 30 K, and the magnetic entropy reaches $R \ln 4$ at about 50 K. This indicates that the first excited doublet is situated at about 50 K from the ground state. In addition, the thermal expansion along the tetragonal [001] direction exhibits a clear negative peak around 25 K, which is also attributed to the magnetic excitations between crystalline electric field (CEF) states. These data, together with the anisotropic magnetic susceptibility, were analyzed on the basis of a CEF model, and splitting energies from the ground state to the first and second excited states were estimated to be 48 and 140 K, respectively. Furthermore, the anisotropy in the high-field magnetization was well explained by the present CEF model with the same parameters, where the saturation moment for $H \parallel [001]$ is found to be determined by the value of $g_J \mu_c$ of the ground state.

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I. INTRODUCTION

Cerium intermetallic compounds often exhibit competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the Kondo effect, which leads to unusual ground states. Depending on the strength of the magnetic exchange interaction $J_{cf}$ between the conduction electron ($c$) and 4$f$ spins, either magnetic or nonmagnetic ground states are observed at low temperatures. Wherever the RKKY interaction is dominant, the magnetic ground state is stabilized by the conduction-electron-mediated indirect exchange interaction between 4$f$-electron moments. The actual magnetic structure depends on the anisotropy of the RKKY interaction and the crystalline electric field (CEF).

With increasing $J_{cf}$, the magnetic moments of the localized 4$f$ electrons are screened by the spin polarization of the conduction electrons, resulting in spin fluctuations and a reduced magnetic moment and transition temperature. A nonmagnetic Fermi-liquid state with strong spin fluctuations is established for large $J_{cf}$ beyond the critical value of $J_c$ at a quantum critical point. In the vicinity of the quantum critical point, a non-Fermi-liquid character and/or unconventional superconductivity have been found, and stimulating experimental and theoretical studies are in progress to clarify the interplay between magnetism and superconductivity.

In addition to this competition, as often observed in cerium Kondo systems, the CEF plays a significant role in determining their thermodynamic and magnetic properties. The CEF analysis provides information about the f levels and the wave functions of the f electron ground state involved in the hybridization effect. The CEF analysis is a starting point for theoretical analyses which extend beyond simple phenomenology. In addition, it was proposed that the CEF potential is itself largely dependent on the hybridization between the localized f-electron states and the conduction band states which are responsible for the heavy-fermion behavior.$^1$

CeAgSb$_2$ crystallizes in the tetragonal ZrCuSi$_2$-type structure ($P4/nmm$) with lattice constants $a=4.363$ Å and $c=10.699$ Å.$^{2,3}$ The characteristic feature of this crystal structure is a sequential stacking of CeSb-Ag-CeSb-Sb layers along the [001] direction, as shown in Fig. 1. The electrical resistivity shows $-\ln T$ dependence with decreasing tem-
suggest that CeAgSb$_2$ is a ferromagnet below almost localized at low temperatures.

measurements performed on a high-quality single crystal of magnetic susceptibility, magnetization, and heat capacity systems. In addition, preliminary inelastic neutron scattering maximum centered around 80 K and a plateau near 20 K. The magnetic structure 5 and a complex antiferromagnetic structure with a resultant ferromagnetic component along the tetragonal unit cell.

With regard to the magnetic structure in the ordered state, neutron powder diffraction experiments done by André et al. suggest that CeAgSb$_2$ is a ferromagnet below $T_c = 9.5$ K with the magnetic moment of 0.33$\mu_B$ aligned parallel to the [001] direction ($c$ axis).$^6$ On the other hand, a simple ferrimagnetic structure$^2$ and a complex antiferromagnetic structure with a resultant ferromagnetic component along [001] (Refs. 3 and 4) are also proposed by bulk magnetic measurements. From the recent muon spin relaxation ($\mu$SR) measurement, Dann et al.$^8$ claim that a simple ferrimagnetic structure is not realistic, because the spectra in both the ordered and paramagnetic states indicate a single crystallographic and magnetic muon site. It is, however, extremely difficult to discriminate between a simple ferromagnetic structure and a complex antiferromagnetic structure with a ferromagnetic net moment.

The low-temperature electronic state has been studied by de Haas–van Alphen (dHvA) experiments,$^9,10$ and it was revealed that CeAgSb$_2$ has large cylindrical but corrugated Fermi surfaces with relatively large cyclotron masses of $(20–30)\hbar$.$^9,10$ These large Fermi surfaces, which occupy about half of the Brillouin zone, are in contrast to small Fermi surfaces of LaAgSb$_2$ and YAgSb$_2$ which have a semimetallic character. These dHvA experiments indicate a quasi-two-dimensional electronic state in CeAgSb$_2$. As stated above, both the electronic and magnetic properties in the single-crystal CeAgSb$_2$ are not explained consistently and not fully understood in spite of intensive experimental efforts. In order to get more insight into the low-temperature electronic and magnetic properties in CeAgSb$_2$, we have performed measurements of the specific heat up to 80 K, the thermal expansion up to 250 K, and in magnetic fields up to 8 T and high-field magnetization up to 50 T.

II. EXPERIMENT

Single crystals were grown by the self-flux method, as described in Ref. 3. Starting materials were 99.999% pure Ce, 99.999% pure Ag, and 99.999% pure Sb. The typical size was $8 \times 5 \times 3$ mm$^3$, being flat in the $\langle 001 \rangle$ plane. The residual resistivity $\rho_0$ and the residual resistivity ratio $\rho_{RT}/\rho_0$ were 0.19 $\mu \Omega$ cm and 430 for the current $J \parallel [100]$, indicating a high-quality sample. The specific heat was measured by the quasiadiabatic heat pulse technique in the temperature range from 0.5 to 80 K. The magnetic susceptibility and magnetization were measured by using a commercial superconducting quantum interference device (SQUID) magnetometer in the temperature range from 1.8 to 300 K and in fields up to 7 T. The measurement of thermal expansion was carried out by using a sensitive three-terminal capacitance method in the temperature range from 4.2 to 250 K. The sample was mounted in a parallel-plate capacitance cell made of oxygen-free high-conductivity copper and placed in a superconducting magnet with a maximum field of 8 T. The high-field magnetization was measured by the standard pickup coil method in fields up to 50 T, which were generated by a long-pulse magnet to avoid eddy current heating of the sample.

III. EXPERIMENTAL RESULTS

A. Specific heat

Figure 2(a) shows the temperature dependence of the specific heat in CeAgSb$_2$ and its reference sample LaAgSb$_2$. The data for CeAgSb$_2$ have a clear jump at $T_{ord} = 9.7$ K, showing a distinctive phase transition, while the displayed data for LaAgSb$_2$ are used for estimation of the magnetic contribution to the specific heat of CeAgSb$_2$. Even above $T_{ord}$, the specific heat of CeAgSb$_2$ is obviously larger than that in LaAgSb$_2$, indicating that there is a significant mag-

FIG. 1. Crystal structure of CeAgSb$_2$. The solid line represents the tetragonal unit cell.
FIG. 2. Temperature dependence of the specific heat of a single crystal of CeAgSb$_2$ (circles) and LaAgSb$_2$ (triangles) (a) and magnetic specific heat $C_{\text{mag}}$ of CeAgSb$_2$ (b). The solid line in panel (b) is a fit using the CEF model (see text).

magnetic contribution derived from Ce$^{3+}$ ions above $T_{\text{ord}}$. The magnetic specific heat $C_{\text{mag}} = C(CeAgSb$_2$) - $C$(LaAgSb$_2$) is plotted in Fig. 2(b). A broad peak centered at about 30 K is found above $T_{\text{ord}}$, which is associated with the Schottky excitations arising from a CEF splitting of the Hund’s-rule ground-state multiplet. The solid line is the calculated magnetic specific heat based on a CEF model, which will be discussed later.

The temperature dependence of the magnetic entropy $S_{\text{mag}}$, which is obtained by integrating the magnetic specific heat divided by temperature $C_{\text{mag}}/T$, is shown in Fig. 3. The magnetic entropy reaches almost $R \ln 2$ at $T_{\text{ord}}$, indicating that the ground state in the CEF scheme of the Ce$^{3+}$ ion is a doublet. Above $T_{\text{ord}}$, $S_{\text{mag}}$ gradually increases and reaches $R \ln 4$ around 50 K. In tetragonal symmetry, the degenerate sixfold levels of the ground-state multiplet of Ce$^{3+}$ split into three doublets, and $\Delta_1$ and $\Delta_2$ are the excitation energies for the first and second excited states, respectively. The entropy change above $T_{\text{ord}}$ suggests that the magnitude of the energy $\Delta_1$ is about 50 K, because the entropy attains a value of $R \ln 4$ at about 50 K.

From the spin-wave theory, the temperature dependence of the magnetic specific heat for ferromagnets and antiferromagnets is proportional to $T^{3/2}$ and $T^3$, respectively, in a temperature range below $T_{\text{ord}}$. The solid line in Fig. 4 is the fitting curve with the form of $C_{\text{mag}} = \gamma T + \Delta T^3$, where $\gamma = 46 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\Delta = 14 \text{ mJ mol}^{-1} \text{ K}^{-4}$, assuming spin-wave excitations in the antiferromagnets. The fitting is rather good below 5 K. On the other hand, the theoretical curve for ferromagnetic excitations can fit to the experimental data only below 1.5 K, as shown in Fig. 4 by a dashed line. The ferromagnetic excitation below 1.5 K is consistent with the ferromagnetic ordering below $T_{\text{ord}}$. It is interesting that the ferromagnetic spin-wave excitation was observed only well below $T_{\text{ord}}$.

B. Thermal expansion

The temperature variations of the thermal expansion of CeAgSb$_2$ along [100] and [001] are shown in Fig. 5. The thermal expansion along [100] gradually decreases with lowering temperature in the whole temperature range measured, except for a weak anomaly at $T_{\text{ord}}$ as shown in Fig. 5(b). In contrast with the above features in [100], the thermal expansion along [001] shows an unusual temperature dependence. The thermal expansion along [001] has a broad minimum around 60 K and increases for further decreasing temperature with a clear kink at $T_{\text{ord}}$. If the thermal expansion is composed of only the lattice contribution, it will only decrease monotonically with decreasing temperature. The negative thermal expansion for [001] indicates the presence of a substantial magnetic contribution associated with Ce$^{3+}$ ions at low temperatures. Recently, Adroja et al. reported similar results of the thermal expansion measurements on a single-crystal CeAgSb$_2$ and suggested that the magnetic contribution is due to the CEF effect.

The temperature dependence of the thermal expansion coefficient $\alpha$, which is defined by $\alpha = d(\Delta V)/dT$, and the specific heat divided by temperature $C/T$ are shown in Fig.
Clear positive and negative peaks of $\alpha$ were observed for $[100]$ and $[001]$, respectively, at the same temperature, where the specific heat exhibits the magnetic transition at $T_{\text{ord}} = 9.7$ K. The initial slope of the pressure dependence of the ordering temperature can be estimated from the Ehrenfest relation by using the values of $\alpha$ and $C/T$ as

$$dT_{\text{ord}}/dp = \frac{V_m \Delta \alpha_V}{\Delta (C/T)},$$

where $V_m$ is the molar volume, and $\Delta \alpha_V$ and $\Delta (C/T)$ are changes of the volume thermal expansion coefficient and the specific heat divided by temperature below $T_{\text{ord}}$. By using the experimental values of $V_m = 1.226 \times 10^{-4}$ m$^3$/mol, $\Delta \alpha_V = -2.6 \times 10^{-5}$ K$^{-1}$, and $\Delta (C/T) = 1.65$ J mol$^{-1}$ K$^{-2}$, we obtain the $dT_{\text{ord}}/dp$ as $-1.9$ K/GPa. This value is comparable to the values of $\sim -0.95$ K/GPa (Ref. 7) and $\sim -1.5$ K/GPa (Ref. 12) estimated from pressure studies on the ac susceptibility and the electrical resistivity, respectively. The minus sign in $dT_{\text{ord}}/dp$ means a suppression of $T_{\text{ord}}$ under pressure, being consistent with hydrostatic pressure experiments.\cite{7,12} The opposite change in $\alpha$ at $T_{\text{ord}}$ suggests an opposite pressure dependence of $T_{\text{ord}}$ when the pressure is applied uniaxially; that is, $T_{\text{ord}}$ will increase and decrease under uniaxial pressure along $[100]$ and $[001]$, respectively.

Next we show in Figs. 7(a) and 7(b) the temperature dependence of the thermal expansion coefficient $\alpha$ up to the maximum temperature measured for $[100]$ and $[001]$, respectively. At high temperatures, the thermal expansion coefficients for both directions show a Debye temperature dependence, characteristic of the phonon contribution. Below 100 K, $\alpha$ for $[100]$ decreases rapidly down to 4.2 K except for the sharp peak at $T_{\text{ord}}$, while for $[001]$, $\alpha$ shows a distinct negative dip at about 25 K, where the Schottky excitation peak was observed at about 30 K in the magnetic specific heat as shown in Fig. 2. This is in agreement with the suggestion that the negative dip in $\alpha$ \cite{7} for $[001]$ is due to the Schottky excitations between the CEF levels.
In order to examine the magnetic field effect, the isofield thermal expansion along [001] was measured in the field parallel to [001]. The result is plotted in Fig. 8. The peak height at $T_{\text{ord}}$ is rapidly suppressed by applying the magnetic field, while the peak position is only slightly shifted to higher temperatures—namely, from $T_{\text{ord}}(H=0) = 9.7$ K to 11.5 K at 8 T. Above $T_{\text{ord}}$, the temperature variations of $\alpha$ in magnetic fields are similar to the zero-field data. It is, therefore, clear that the origin of the broad negative peak is hardly affected by a magnetic field as high as 8 T.

C. High-field magnetization and magnetic phase diagram

The magnetization of CeAgSb$_2$ below 7 T was measured by a SQUID magnetometer. The magnetization at 2 K along [001] saturates at a very low field with a saturation moment of about $0.4 \mu_B$ and remains nearly constant up to 7 T. When the field is removed, it has a remanent magnetization of $0.4 \mu_B$. On the other hand, the magnetization along [001] increases almost linearly up to about $1.2 \mu_B$ around 3 T and slowly increases at higher fields. These values are in good agreement with a previous study. To understand this anomalous magnetization curve, we have measured the high-field magnetization by using a long-pulse magnet. The high-field magnetization curves for both directions at 1.5 and 20 K are shown in Fig. 9. The magnetization along [100] at 1.5 K increases linearly but suddenly changes its slope at around 3 T. For further increasing the magnetic field, the magnetic moment gradually develops up to 50 T, reaching $1.65 \mu_B$ at the maximum field. It is clear that higher fields are necessary to saturate the magnetization for $H \parallel [100]$. This characteristic feature is typical of an antiferromagnetic compound. At 20 K, which is above $T_{\text{ord}}$, the kink in the magnetization at 1.5 K disappears, and the magnetization increases monotonically to $1.57 \mu_B$ at 50 T. The magnetization along [001] is more intriguing. The magnetization at 1.5 K remains nearly constant at high fields, showing a saturation moment of about $0.4 \mu_B$. Furthermore, the magnetization at 20 K increases almost linearly and exceeds $0.4 \mu_B$ in the field above 36 T. The reason for this crossing of the magnetization curves will be discussed later.

Figure 10 shows the differential magnetization $dM/dH$ for $H \parallel [100]$ at several temperatures. A steplike anomaly in the $dM/dH$ curves corresponds to a slope change in the magnetization as seen in Fig. 9. This anomaly shifts to lower fields with raising the temperature and disappears at 10.1 K which is just above $T_{\text{ord}}$. The transition fields are determined at the midpoint of the anomaly as shown by arrows and plotted in the $H-T$ space as shown in Fig. 11 by open circles. Open squares represent the magnetic field values where the magnetization isotherm along [100], measured by a SQUID

![FIG. 8. Temperature dependence of the thermal expansion coefficient along [001] in magnetic fields along [001].](image)

![FIG. 9. High-field magnetization curves at 1.5 and 20 K for $H \parallel [100]$ and [001].](image)

![FIG. 10. Differential magnetization curves for the field along [100] in CeAgSb$_2$ at selected temperatures.](image)
magnetometer, changes its slope. These transition points can be traced by one line which is connected smoothly to $T_{\text{ord}} = 9.7$ K at zero magnetic field. This means that these transitions in the magnetization along $\hat{z}$ are related to the magnetic ordering at $T_{\text{ord}}$.

In contrast to $H \parallel [100]$, the transition temperature slightly shifts to a higher temperature when we apply a magnetic field along $\hat{z}$ as shown by solid triangles. This behavior of the transition temperature in the magnetic field seems to be consistent with the ferromagnetic transition at $T_{\text{ord}}$. It is, however, not clear why the magnetization curve as well as the magnetic phase diagram shows different characteristics depending on the crystallographic axis.

IV. ANALYSES AND DISCUSSION

A. Estimation of the lattice contribution to the thermal expansion

In order to analyze the thermal expansion coefficient, we should know the temperature dependence of the lattice contribution which is expressed by the Grüneisen function. According to the Grüneisen relation, the thermal expansion coefficient is related to the specific heat as

$$\alpha = \frac{\Gamma C_V}{B_T V}.$$  \hspace{1cm} (2)

where $\Gamma$ is the Grüneisen parameter, $B_T$ the bulk modulus, and $C_V$ the specific heat at constant volume. This equation means that the temperature dependence of the thermal expansion is approximately the same as that of the specific heat. On the basis of the Debye model, the lattice specific heat is given by

$$C_V = 9Nk_B\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\Theta_D/T} \frac{x^5}{(e^x-1)^2} dx,$$  \hspace{1cm} (3)

where $N$ is the number of atoms, $k_B$ the Boltzmann constant, and $\Theta_D$ the Debye temperature.

In order to estimate the value of $\Theta_D$, we fitted Eq. (3) to the specific heat data of LaAgSb$_2$ as shown in Fig. 12(a). Over all specific heat data of LaAgSb$_2$ is well expressed by Eq. (3), and the Debye temperature is thus estimated to be 196 K. By using the same Debye temperature, we calculated the temperature dependence of the resistivity by using the expression

$$\rho(T) = \rho_0 + A\frac{T^5}{\Theta_D/T} \int_0^{\Theta_D/T} \frac{x^5}{(e^x-1)(1-e^{-x})} dx,$$  \hspace{1cm} (4)

where $\rho_0$ is the residual resistivity, $A$ is a numerical constant, and the second term is due to the phonon-assisted electron scattering. As shown in Fig. 12(b), $\rho(T)$ for YAgSb$_2$ (Ref. 3) is well described by Eq. (4) with $\Theta_D = 196$ K. We have used this value as the Debye temperature for the lattice contribution to the thermal expansion, although this value is slightly smaller than the previously reported values of $\Theta_D = 249$ K (Ref. 5) and 220 K (Ref. 10) estimated from the low-temperature specific heat data.

B. Crystalline electric field analysis

The specific heat and thermal expansion coefficient show broad peaks with a long tail towards higher temperatures as shown in Figs. 2 and 7. These features are probably due to the Schottky excitations between the CEF levels of Ce$^{3+}$. ln order to estimate the value of $\Theta_D$, we fitted Eq. (3) to the specific heat data of LaAgSb$_2$ as shown in Fig. 12(a). Over all specific heat data of LaAgSb$_2$ is well expressed by Eq. (3), and the Debye temperature is thus estimated to be 196 K. By using the same Debye temperature, we calculated the temperature dependence of the resistivity by using the expression

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where $\rho_0$ is the residual resistivity, $A$ is a numerical constant, and the second term is due to the phonon-assisted electron scattering. As shown in Fig. 12(b), $\rho(T)$ for YAgSb$_2$ (Ref. 3) is well described by Eq. (4) with $\Theta_D = 196$ K. We have used this value as the Debye temperature for the lattice contribution to the thermal expansion, although this value is slightly smaller than the previously reported values of $\Theta_D = 249$ K (Ref. 5) and 220 K (Ref. 10) estimated from the low-temperature specific heat data.
molecular field contribution is given as follows. The CEF Hamiltonian for tetragonal symmetry can be expressed as

$$\mathcal{H}_{\text{CEF}} = B_1^2 O_2^0 + B_2^2 O_4^0 + B_4^2 O_4^4,$$  \hspace{1cm} (5)

where $B_1^m$ and $O_4^m$ are the CEF parameters and the Stevens operators, respectively.\textsuperscript{13,14} Due to the CEF effect, the sixfold-degenerated $4f$ levels are split into three doublets with excitation energies $\Delta_1$ and $\Delta_2$ from the ground to the first and second excited states, respectively. In this case, the Schottky specific heat can be written as

$$C_{\text{sch}} = \left( \frac{R}{(k_B T)^2} \right) \left\{ \frac{\Delta_1 + \Delta_2}{k_B T} \left[ \sum_{n=1}^3 \frac{\mu_n^2 e^{-\Delta_n / k_B T}}{Z} \right] - \frac{\Delta_1 + \Delta_2}{k_B T} \left[ \sum_{n=1}^3 \frac{E_n e^{-E_n / k_B T}}{Z} \right] \right\}, \hspace{1cm} (6)$$

where $\mu_n$ is defined by $\langle n | O_2^0 | n \rangle$. $E_n$ and $| n \rangle$ are the $n$th eigenvalue and eigenfunction, respectively, and $Z = \sum_n e^{-E_n / k_B T}$. $B_i (i=[100]$ and $[001]$) is a fitting parameter for the principal axis. The total thermal expansion coefficient above the ordering temperature is expressed by the sum of the lattice and magnetic parts as

$$\alpha_{\text{total}} = \alpha_{\text{lattice}} + \alpha_{\text{CEF}} \hspace{1cm} (i=[100]$ and $[001]). \hspace{1cm} (8)$$

The CEF parameters were determined so as to reproduce the specific heat and thermal expansion as well as susceptibility data, which are in agreement with the preliminary results of inelastic neutron scattering experiments.\textsuperscript{17} The solid lines in Figs. 2, 13, and 14 show the calculated curves by using the CEF parameters listed in Table I. The magnetic specific heat above $T_{\text{ord}}$ is well explained by the CEF model as shown in Fig. 2. Furthermore, the estimated energy splitting $\Delta_1 = 48$ K is consistent with the entropy change shown in Fig. 3, since the magnetic entropy reaches $R \ln 4$ around 50 K.

As regards to the temperature dependence of the thermal expansion coefficient, characteristic features can be ex-

\hspace{1cm} \hspace{1cm}

![FIG. 13. Temperature dependence of the thermal expansion coefficient of CeAgSb$_2$ along (a) [100] and (b) [001]. Dashed and dash-dotted lines show the magnetic ($\alpha_{\text{CEF}}$) and the lattice ($\alpha_{\text{lattice}}$) contributions, respectively. Solid lines are the sum of $\alpha_{\text{lattice}}$ and $\alpha_{\text{CEF}}$. Fitting parameters are ($\Gamma B_V V_{\text{[100]}} = 1.4 \times 10^{-3}$ molJ and $B_{[100]} = 5.7 \times 10^{-5}$ for [100] and ($\Gamma B_V V_{\text{[001]}} = 1.4 \times 10^{-3}$ molJ and $B_{[001]} = -2.8 \times 10^{-4}$ for [001].](http://example.com/fig13)
The magnetic susceptibility in CeAgSb₂ follows the Curie-Weiss law in the temperature range above 100 K, but the estimated effective moment is somewhat smaller than the theoretical value of 2.54 μ_B/Ce for Ce³⁺: namely, 2.47 μ_B/Ce for [100] and 2.48 μ_B/Ce for [001]. This is why the slope of the experimental inverse susceptibility curve above 100 K becomes larger than that of the theoretical one.

It is noted that CEF excitations in CeAgSb₂ were observed by recent inelastic neutron scattering experiments. The present CEF level scheme is consistent with the observed excitation energies of 5.1 meV (~59 K) and 12.4 meV (~144 K). Furthermore, the small mixing between |±3/2⟩ and |±5/2⟩ states is also consistent with the fact that the observed excitation intensity at 12.4 meV is very weak compared to that at 1.5 meV. From this analysis, it is found that the CEF ground state in CeAgSb₂ is |±1/2⟩, and the first and second excited levels are dominated by |±3/2⟩ and |±5/2⟩ states, respectively.

C. Magnetization based on the CEF model

Next we discuss the magnetization on the basis of the CEF model. The magnetization can be calculated by

\[
M_i = g_J \mu_B \sum_n \left| \langle n|J_i|n \rangle \right| \frac{e^{-E_n/k_B T}}{Z} \quad (i = x, y, \text{ and } z).
\]

(11)

The eigenvalue \(E_n\) and the eigenfunction \(|n⟩\) are determined by diagonalizing the total Hamiltonian

\[
\mathcal{H} = \mathcal{H}_{\text{CEF}} - g_J \mu_B J_i (H_i + \lambda_i M_i),
\]

(12)

where \(\mathcal{H}_{\text{CEF}}\) is given by Eq. (5), the second term is the Zeeman term, and the third one is from the molecular field. In Fig. 15, we show the calculated magnetization curves by using the same CEF parameters as in Table I and replot the experimental curves by thick solid lines which were already shown in Fig. 9. For \(H||[100]\), the calculated magnetization shows a gradual increase up to about 100 T and almost saturates at higher fields. On the other hand, the calculated magnetization for \(H||[001]\) at 1.5 K indicates three steps as shown in Fig. 15(b). These step magnetizations are due to the level crossing in the CEF scheme. The magnetic field dependence of CEF energy levels for \(H||[100]\) and [001] is shown in Figs. 16(a) and 16(b), respectively. When the magnetic field is applied along [001], degenerate levels are split and

![Graph](image)

FIG. 14. Temperature dependence of the inverse magnetic susceptibility in CeAgSb₂. Solid lines are the calculated curves based on the CEF model.

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**TABLE I.** CEF parameters, energy level schemes, and corresponding wave functions for CeAgSb₂.

<table>
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<th>CEF parameters</th>
<th>(B^0_2) (K)</th>
<th>(B^0_4) (K)</th>
<th>(B^4_4) (K)</th>
<th>(\lambda_{100}) (emu/mol)⁻¹</th>
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<table>
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<th>Energy levels and wave functions</th>
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the energy of each state changes almost linearly with increasing magnetic field except for a crossover around 40 T between the first and second excited states. The metamagnetic transitions at 87 and 148 T in Fig. 15 are due to the 4f-level crossing in the ground state, where the wave function changes from a \( u_2^{1/2} \) to \( u_2^{3/2} \) and from a \( u_2^{3/2} \) to \( u_2^{5/2} \), respectively, as shown by two arrows in Fig. 16. Since the energy of the ground state decreases linearly with increasing field except the slope change at transition fields, the magnetization stays constant below and above the transition fields. The value of the magnetization plateau corresponds to the \( gJ_z \) value for each state: that is, 0.43, 1.29, and 2.14 for the first, second, and third steps, respectively. At 20 K, the magnetization increases almost linearly, crossing the midpoint of the magnetization plateau at 1.5 K.

From the comparison between the calculated and experimental curves, it is concluded that the observed anisotropy in the magnetization curve is determined by the CEF effect. In particular, the observed crossing behavior of the magnetization for \( H \parallel [001] \) around 40 T is well explained by the calculated magnetization. Furthermore, it should be noted that the value of the saturation moment at 1.5 K for \( H \parallel [001] \) agrees very well with the calculated value, although it is in the ordered state. This indicates that the saturation moment of about 0.4\( \mu_B \) is defined by the \( gJ_z \) value of the ground state.

As for the ground-state magnetic structure, neutron scattering experiments suggest that the magnetic moments are oriented ferromagnetically along \( [001] \) with the value of 0.3\( \mu_B \)–0.75\( \mu_B \). On the other hand, complicated structures such as a ferrimagnetic and a canted state have also been suggested by bulk measurements.3–5 The observed magnetization along \( [001] \) at 1.5 K saturates at very low field and remains almost constant up to 45 T, showing about 0.4\( \mu_B \). It seems, therefore, difficult to consider the complicated structures for the ordered state. The rather small ordered moment in CeAgSb2 may also be due to the CEF effect. Nevertheless, it is still not clear why the ordered magnetic moments are aligned along the \( [001] \) direction and the magnetization for \( H \parallel [100] \) shows antiferromagnetic features. Precise neutron scattering experiments are necessary to understand the ground-state magnetic structure as well as the real nature of the spin-wave excitation, and these are in progress.

V. CONCLUSION

We have studied the electronic and magnetic properties of a single crystal of CeAgSb2 by measuring the specific heat, thermal expansion, and high-field magnetization. In the paramagnetic phase, the specific heat and thermal expansion show a broad peak with a long tail towards higher temperatures around 30 K and 25 K, respectively. These data as well as the susceptibility are analyzed on the basis of the CEF model with splitting energies \( \Delta_1 = 48 \) K and \( \Delta_2 = 140 \) K from the ground state to first and second excited states, respectively. In the ordered state, the high-field magnetization along [100] shows a kink around 3 T and gradually increases up to 50 T, reaching 1.65\( \mu_B \). On the other hand, the magnetization along [001] saturates at about 0.4\( \mu_B \) and remains almost constant in high fields up to 45 T. This saturation moment is in good agreement with the value of \( gJ_z = 0.43 \) for \( |\pm 1/2| \) of the ground state in the CEF scheme. In addition, the anisotropy of the magnetization is also well explained by the CEF model with the same parameters.
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