

試料作製・評価による希土類化合物の研究
—少数キャリア系希土類プニクタイト Yb_4As_3 及び
希土類水素化物 $\text{SmH}_{2+\delta}$ を例として—

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**The research of sample preparation and measurement of
physical properties of rare-earth compounds:
As examples on the low carrier rare-earth pnictide Yb_4As_3 ,
and the rare-earth hydride $\text{SmH}_{2+\delta}$**

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Abstract

Physical properties were investigated for Yb_4As_3 and $\text{SmH}_{2+\delta}$. In the case of Yb_4As_3 , the Sommerfeld coefficient $\gamma = 200 \text{ mJ}/(\text{K}^2 \text{ mole})$ of Yb_4As_3 does not originate from impurities. The change of γ is observed when the specific heat is measured in a magnetic field of 1 T. The Korringa law ($T_1T=\text{constant}$) holds only in the narrow temperature range between 20 K and 10 K. Their physical properties of Yb_4As_3 cannot be described by a simple Fermi liquid picture. In the case of bulk $\text{SmH}_{2.16}$, the temperature dependence of the magnetic susceptibility and of the specific heat in the paramagnetic region can be described by assuming all Sm ions are Sm^{3+} ; ground state Γ_8 . The Cp/T exhibits an antiferromagnetic spin wave and that the Sommerfeld coefficient γ is $150 \text{ mJ}/(\text{K}^2 \text{ mole})$. In the case of $\text{SmH}_{2+\delta}$ films, the reflectivity shows a minimum at 1–2 eV, which is possibly due to a plasma edge. The minimum show a red shift as the H/Sm ratio increases. The transmittance has a maximum at about 1 eV. The line shape of the optical conductivity cannot be explained in terms of a simple single carrier model. In the range 0.25–0.6 eV, the relaxation time increases as δ increases.

Introduction

Electrical and optical properties of compounds classify materials into metals, semiconductors, and insulators. These physical properties are usually explained by the band model. However, this model cannot explain physical properties of compounds with 3d and or 4f electrons, because correlation interactions between electrons are not included.

Rare-earth compounds with 4f electrons show interesting properties due to correlations, such as magnetism, the dense Kondo effect, heavy fermions, valence fluctuations, and superconductivity.

In some rare earth compounds such as a pnictide, Yb_4As_3 , and a hydride, $\text{SmH}_{2+\delta}$, it is difficult to obtain their intrinsic physical properties due to difficulty of sample preparations for good samples. In this study, intrinsic physical properties were investigated using samples obtained by a sealed tungsten crucible for Yb_4As_3 and thin films on a quartz substrate for $\text{SmH}_{2+\delta}$.

Yb_4As_3 and related compounds

Yb_4As_3 exhibits a heavy fermion behavior (e.g., its Sommerfeld coefficient γ is about 200 mJ/(K² mole) despite an extremely low carrier concentration of 0.1% per Yb^{3+} ion. Yb_4As_3 also exhibits charge ordering (the ratio of Yb^{2+} to Yb^{3+} ions is 3:1) under T_c in the room temperature regime.

In this study, we examined the sample dependence of the physical properties of Yb_4As_3 (Sample No. 3, 4, 5, 11, 12 and 14). The physical properties of Yb_4As_3 , $\text{Yb}_4\text{As}_{3-x}\text{P}_x$, $\text{Yb}_4\text{As}_{3-x}\text{Sb}_x$, Yb_4Sb_3 , and Yb_4Bi_3 were measured to investigate the change of hybridization between the conduction and the 4f electrons.

In the case of Yb_4As_3 , a main cause of sample dependence for their physical properties is a variation of the arsenic (As) content in single

crystals, which is small in polycrystalline samples. The residual resistivity ρ_0 increases and the ratio of the maximum resistivity ρ_{max} to the residual resistivity (ρ_{max}/ρ_0) decreases as the charge order-disorder transition temperature T_c of a sample decreases. The Hall coefficient for a sample with a high T_c is large in the neighborhood of T_c .

For Yb_4As_3 , C/T shows a linear function of T^2 in the temperature range 7.1-17.3 K. The Sommerfeld coefficient γ_{HT} is 240-250 mJ/(K² mole). γ_{HT} exhibits no sample dependence. For temperatures below 7.1 K, the straight line (a linear function of T^2) change the gradient. The Sommerfeld coefficient γ_{LT} is 170-200 mJ/(K² mole); it has a weak sample dependence. Sample No.12 and 14 (γ_{LT} is 200 mJ/(K² mole)) are stoichiometrically good samples. Based on these results, the large γ_{LT} of Yb_4As_3 is considered not to originate from lattice defects, but rather it is considered to be an inherent property of the material.

Despite the Kondo temperature being about 50 K, which was estimated from magnetic susceptibility measurements and the Sommerfeld coefficient γ , the change of specific heat is observed when the specific heat is measured in a magnetic field of 1 T.

The Korringa law ($T_1T=\text{constant}$) holds only in the narrow temperature range between 20 K and 10 K. $1/T_1T$ increases with decreasing temperature below 10 K. This implies that the increase in the susceptibility at low temperatures is an intrinsic property of Yb_4As_3 . The properties of Yb_4As_3 cannot be described by a simple Fermi liquid picture.

The NQR resultant and specific heat measurements in a magnetic field reveal that Yb_4As_3 is not a heavy fermion. The Yb^{3+} ion in Yb_4As_3 forms a one-dimensional $S=1/2$ Heisenberg antiferromagnetic chain. This one-dimensional antiferromagnetic dispersion explains the γT term of the specific heat. The γT term of the specific heat

of $\text{Yb}_4\text{As}_{3-x}\text{Sb}_x$ is similarly understood.

The Sommerfeld coefficient γ of Yb_4Bi_3 is about $10 \text{ mJ}/(\text{K}^2 \text{ mole})$, which indicates Pauli paramagnetism (i.e., a normal metal). The Sommerfeld coefficient γ of Yb_4Sb_3 is about $40 \text{ mJ}/(\text{K}^2 \text{ mole})$, which may indicate valence fluctuations. This result is consistent with the measured magnetic susceptibility.

$\theta_{\text{D(LT)}}$, which is found by extrapolating the T^2 dependence of C/T from the temperature range 2-7 K, does not give a reasonable Debye temperature for Yb_4As_3 , but $\theta_{\text{D(HT)}}$, which is found by extrapolating from the temperature range 10-17 K, gives a reasonable value. The Debye temperature $\theta_{\text{D(HT)}}$ increases and β_{HT} decreases as the pnictogen weight of Yb_4X_3 (X=As, Sb or Bi) decreases.

SmH_{2+δ}

The rare-earth hydride exhibits various electronic states such as metallic, semiconductive, and insulating ones depending on the hydrogen content. The hydrogen content also affects its magnetic property.

Stoichiometric SmH_2 has an antiferromagnetic (AF) structure below the Neel temperature T_N . The temperature dependence of the magnetic susceptibility reveals that T_N is 9.7 K and that all Sm ions have a valence of +3. A change in magnetic property of $\text{SmH}_{2+\delta}$ is expected for $\delta > 0$ and $\text{SmH}_{2+\delta}$ may be a mixed valence compound. The ground state due to crystalline field of $\text{SmH}_{2+\delta}$ is indistinct and its Sommerfeld coefficient γ was not determined.

To obtain a better understanding of the material characteristics, the present study investigates the thermal and magnetic properties of bulk $\text{SmH}_{2+\delta}$. So far, only insufficient spectroscopic data has been obtained for bulk $\text{SmH}_{2+\delta}$, because it is difficult to synthesize a bulk $\text{SmH}_{2+\delta}$ for optical measurements, which reveal important information about its electronic states. Hence, we

prepared samarium dihydride thin films for optical measurements. The inverse susceptibility of bulk $\text{SmH}_{2.16}$ has small kinks at 15.2 K and 10.6 K and an inflection point at 7.0 K. The temperature dependence of the magnetic susceptibility in the paramagnetic region can be described by assuming the following: Sm^{3+} ; ground state: Γ_8 ; crystal field splitting: $\Delta=200 \text{ K}$; transition energy: $\Delta E_j=1900 \text{ K}$ between J multiplet terms ($J=5/2, J=7/5$).

The specific heat of $\text{SmH}_{2.16}$ exhibits three peaks at 7.1 K, 10.8 K and 15.9 K. The temperature dependence of the specific heat in the paramagnetic region can be described by assuming the following: all Sm ions are Sm^{3+} ; ground state: Γ_8 ; crystal field splitting: $\Delta=200 \text{ K}$; transition energy: $\Delta E_j=1400 \text{ K}$ between J multiplet terms ($J=5/2, J=7/5$). The transition energy for the magnetic susceptibility ($\Delta E_j=1900 \text{ K}$) is larger than $\Delta E_j=1400 \text{ K}$, which is estimated from the NMR Knight shift. Below 7.1 K, C_p/T is a linear function of T^2 , indicating that $\text{SmH}_{2.16}$ exhibits an antiferromagnetic spin wave and that the Sommerfeld coefficient γ is $150 \text{ mJ}/(\text{K}^2 \text{ mole})$. The magnetic entropy is 55% of $2R \log 2$ at 15.9 K, which is the theoretical value of the ground state Γ_8 .

$\text{SmH}_{2+\delta}$ spectroscopic data was obtained. Each reflectivity has a minimum at 1.3-2.4 eV, which is possibly due to a plasma edge. The reflectivities minima are red shifted as the H/Sm ratio increases. The samples transmit light slightly at photon energies of 0.4-3.0 eV. All the samples have a transmittance maximum at about 1 eV. The optical gap between the H1s-like state of the T site and the Sm5d-like state is 2.6 eV, whereas that between the H1s-like state of the O site and the Sm5d-like state is 1.5 eV.

For all samples, the temperature dependence of the resistivity is metallic. In particular, $\text{SmH}_{2.57}$ shows a resistivity minimum at around 30 K. When the temperature is reduced below 30 K, the resistivity has a local maximum at 10 K (which is close to the Neel temperature) and then it reaches

another minimum at 4 K. When the temperature is increased, the resistivity has a local maximum at 14 K.

The optical conductivities obtained from

Kramers-Kronig analysis cannot be explained in terms of a simple single-carrier model. The relaxation time becomes large when the H/Sm ratio approaches the metal-insulator transition region.