Magnetic and transport properties of Yb{T}2Al_{20} (T = Ti, V and Cr)

Ryuji Higashinaka, Akihiro Nakama, Makoto Ando, Makoto Watanabe, Yuji Aoki and Hideyuki Sato
Graduate School of Science, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan
E-mail: higashinaka@phys.metro-u.ac.jp

Abstract. The magnetic and transport properties of single crystalline Yb{T}2Al_{20} (T = Ti, V and Cr) grown by Al self-flux method were investigated. All compounds show weakly-temperature dependent Pauli paramagnetic behavior in the DC susceptibility and show normal metallic behavior without any noticeable shoulders and peaks in the temperature dependence of resistivity. From these measurements, the valence state of Yb ions is expected to be close to divalent.

The physics of cage-like compounds such as filled skutterudites and clathrate compounds has attracted much attention in the past 10 years because of their wide variety of strongly correlated electronic properties attributed to their crystal structures[1, 2, 3]. In these systems, because the rare earth ion with 4f-electrons is surrounded by the large number of cage ions, a strong hybridization between the conduction electrons and 4f electrons of the rare earth ion is expected. Also, because this site has a high cubic point symmetry, small crystal electric field (CEF) effects are expected. These characteristics induce interesting properties of strongly correlated electron system such as novel superconductivity, heavy fermion behavior, multipolar ordering and so on.

Among the cage-like systems, RT_2X_{20} (R = rare earth, T = transition metal, X = Zn, Al) is a new candidate. In these compounds, similarly to other cage-like compounds, the R ions occupy their own single unique crystallographic site with the polyhedron of 16 X atoms surrounding it (Fig.1(a))[4, 5, 6, 7, 8]. In addition to such cage-like structure, T site atoms constitute a network of corner-shared tetrahedra (the pyrochlore lattice) with strong geometrical frustration (Fig.1(a)). In this sense, RT_2X_{20} is a rare system in which two characteristic crystal structures coexist. Although the systems with cage-like or geometrically frustrated structure show interesting physical properties, there has been reported little studies for the system containing both structures.

Since the discovery of RT_2X_{20} compounds, X = Zn compounds have been intensively studied[9, 10, 11]. One of the most important results of the recent studies on these compounds is the especially enormous Sommerfeld coefficient of 7.9 J/mol K^2 of YbCoZn_{20}[9]. In order to investigate the origin of the enormous γ, systematic and comparative studies of magnetic, transport and structural properties of the Zn- and Al-based compounds are essential. In contrast to the Zn-based compound, although RT_2Al_{20} compounds had been discovered earlier by Niemann and Jeitschko[5], only limited works have been reported on them mainly about the crystal growth technique and structural determination. On the Yb-compounds, only the lattice
constant of YbTi$_2$Al$_{20}$ was reported in ref. [5] and there are no other reports on the physical properties of the Yb-compound. In order to investigate the nature of YbTi$_2$Al$_{20}$ compounds in more detail, further investigation especially into the magnetic and transport properties in the transition metal series of the Yb-compound are important. In this work, we prepared single crystals of YbTi$_2$Al$_{20}$ ($T = Ti, V, Cr$) and investigated magnetic and transport properties of these materials.

Single crystals of Yb(Ti, V, Cr)$_2$Al$_{20}$ have been prepared by the Al self-flux method from the starting elements, chips of Yb(3N), powders of Ti(5N), V(4N) or Cr (4N) and grains of Al(4N) at the atomic ratio of 1:2:40. These mixtures were placed in an alumina crucible and they were sealed in an evacuated quartz tube. These sealed tubes were heated up to 1050°C, kept for 2 hours, then cooled down to 750°C for 45 hours. The samples were removed from the furnace and the excess Al was spun off in a centrifuge. Small amount of residual Al-flux on the crystals were removed by etching with 3 vol% HCl or NaOH in H$_2$O for 2 hours in a ultrasonic bath. The quality of the samples was checked using a powder x-ray diffractometer with Co-Kα radiation (Fig. 1(b)). All of the peak are indexed by the Miller’s indices of the CeCr$_2$Al$_{20}$ type structure with cubic $Fd\bar{3}m$ symmetry and absence of any impurity phases was confirmed. From these results, the lattice parameters $a$ for YbTi$_2$Al$_{20}$ ($T = Ti, V, Cr$) are evaluated to be 14.6841(2)Å, 14.5334(8)Å and 14.4466(3)Å, respectively. The parameter $a$ of YbTi$_2$Al$_{20}$ is consistent to the previous report of polycrystals [5]. The crystallographic orientations of the single crystals were determined by the back Laue x-ray scattering technique. Typical size and mass of measured single crystals were about 0.5 mm and about 3 mg, respectively. The DC magnetization was measured using a Quantum Design MPMS down to 2 K and up to 7 T along the [110] direction. The resistivity was measured using a homemade cryostat down to 4 K.

In Fig. 2(a), we show the temperature dependence of the DC susceptibility, $\chi(= M/H)$, for YbTi$_2$Al$_{20}$ ($T = Ti, V$ and Cr) at 1 T. All the compounds exhibit Pauli paramagnetic susceptibility. This behavior indicates that for all compounds the valence of Yb ion is close to divalent. However, because there are weak temperature dependence in $\chi(T)$, it is possible that a small part of the 4f levels are unoccupied and Yb$^{3+}$ contributions remain to some extent. This

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Crystal structure of $RT_2X_{20}$ compound. $R$ ion is surrounding by 16 $X$ ions. T ions form the corner shared tetrahedral network named pyrochlore latticece. (b) X-ray powder diffraction pattern of YbV$_2$Al$_{20}$ using Co-Kα radiation. For main peaks, the Miller’s indices of cubic $Fd\bar{3}m$ symmetry for main peaks are shown.}
\end{figure}
may indicate the possibility of valence fluctuation of Yb ions. However, it is difficult to estimate the degree of c-f hybridization only by our present experimental results. The upturn at lower temperatures in all susceptibility data is expected to be the contributions from paramagnetic impurity phases because its value is very small. The values of Pauli paramagnetic susceptibility extrapolated to 0 K, \( \chi(0) \) (0.5 \( \sim \) 1.0 \( \times \) \( 10^{-3} \) emu/mol) are larger than those of normal metals (\( \sim \) 10\(^{-5} \) emu/mol) and almost comparable to those of La compounds without 4\( f \) electrons (\( \sim \) 0.5 \( \times \) \( 10^{-3} \) emu/mol: data not shown). These magnetic properties are very different from those of the Zn-based compounds that show strongly correlated heavy fermion behavior.

In Fig. 2(b), we show the temperature dependence of the resistivity for Yb\( T \)\( _2 \)Al\( _{20} \) (\( T = \) Ti and V) at 0 T. Their resistivity at room temperature (60 \( \sim \) 100 \( \mu \)\( \Omega \) cm) and the residual resistivity ratio \( \rho(300K)/\rho(4.2K) \) (\( \sim \) 20) are similar to those of the Zn-based compounds[9]. However, the temperature dependence is qualitatively different. For Yb\( Ti_2 \)Al\( _{20} \) and Yb\( V_2 \)Al\( _{20} \), \( \rho \) monotonously decreases with decreasing temperature down to the lowest investigated temperature without any shoulder or peak structures at low temperatures which are observed in the Zn-based compound. These normal metallic behaviors are consistent with the Pauli paramagnetic susceptibility, and are also an indication of almost Yb\(^{2+} \) state in the Al-based compounds. Usually, the cell volume with Yb\(^{2+} \) ions is larger than that with Yb\(^{3+} \) ions. Therefore, the positive deviation of the cell volume for Yb\( Ti_2 \)Al\( _{20} \) in the \( RTi_2 \)Al\( _{20} \) series reported in Ref.[5] is consistently understood based on the lanthanoid contraction. Similarly, the lattice parameters of the other two compounds evaluated from our powder X-ray diffraction patterns also show the positive deviation from the lanthanoid contraction line of the \( RTi_2 \)Al\( _{20} \) series.

In summary, we has studied the magnetic and transport properties of single crystalline Yb\( T \)\( _2 \)Al\( _{20} \) (\( T = \) Ti, V, and Cr). From their nonmagnetic metallic behavior, we concluded that the valence of Yb ions is close to 2+ in these compounds. The weakly-temperature dependent susceptibility indicates the possibility of valence fluctuation of Yb ions. Considering the cage-like structure of the present system, this feature may originate from hybridization between 4\( f \) electron and conduction electrons, leading to a Kondo temperature of the order of a few hundred Kelvin corresponding to the weak T-dep. structure in \( \chi(T) \). In order to examine this scenario, electronic structure studies (by PES and others) are needed.

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**Figure 2.** (a) Temperature dependence of DC susceptibility \( \chi \) of Yb\( T \)\( _2 \)Al\( _{20} \) (\( T = \) Ti, V and Cr) for the fields of 1 T applied parallel to the [110] direction. (b) Temperature dependence of resistivity \( \rho \) of Yb\( T \)\( _2 \)Al\( _{20} \) (\( T = \) Ti and V) at 0 T.
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