Structure and properties of EuAl$_2$Si$_2$, EuAl$_2$Ge$_2$, YbAl$_2$Si$_2$ and YbAl$_2$Ge$_2$

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March 04, 2002

Abstract

LnAl$_2$X$_2$ (Ln=Eu, Yb; X=Si,Ge) compounds are synthesized by heating the elements at 1070–1270 K. They are observed to crystallize in the CaAl$_2$Si$_2$-type structure (space group P3m1) with lattice constants (Å): YbAl$_2$Ge$_2$: $a=4.179$, $c=7.069$. EuAl$_2$Ge$_2$: $a=4.214$, $c=7.320$. EuAl$_2$Si$_2$: $a=4.181$, $c=7.259$. Magnetic susceptibility measurements of EuAl$_2$Si$_2$ and EuAl$_2$Ge$_2$ has shown paramagnetic behavior above 50 K with experimental magnetic moments of 7.82 $\mu_\beta$/Eu and 7.90 $\mu_\beta$/Eu respectively indicating divalent Eu. Antiferromagnetic behavior is also detected at $T_N=35.5$ for EuAl$_2$Si$_2$ and at $T_N=27.5$ for EuAl$_2$Ge$_2$. A typical behavior of an intermediate-valent compound is observed for YbAl$_2$Si$_2$. A linear dependence of the inverse of susceptibility on temperature has been seen between 100 and 300 K with a reduced moment of 2.57 $\mu_\beta$/Yb. A strong negative Curie temperature of 382 K is obtained. LMTO band structure calculations and experimental results confirm that all compounds are metallic between 8 and 320 K.
1. Introduction

$AM_2X_2$ compounds ($A=$ rare- or alkaline earth metal; $M=$metal; $X=$main group 3-6 element) favorably crystallize in the ThCr$_2$Si$_2$ structure [1]. In contrast to this, the metallic aluminum silicides and germanides LnAl$_2$X$_2$ (Ln=rare-earth metal, $X=Si$, Ge) crystallize in the trigonal CaAl$_2$Si$_2$-type structure [1]. The band gap of LnAl$_2$X$_2$ is vanishingly small when the electronegativity difference of the atoms Al$_2$X$_2$ is small [2]. Therefore, the surplus electron does not destabilize the structure as it would do if the energy gap is present. So the metallic behavior of LnAl$_2$X$_2$ is, not a result of the surplus electron, just the electronic structure itself is that of a metal. In other words, every compound $AAl_2X_2$ with $X=Si$ or Ge and CaAl$_2$Si$_2$ structure is expected to be metallic, regardless the valence of the base metal $A$.

In contrast to the pure trivalent rare earth metals, europium and ytterbium have an enhanced stability of the divalent states (4f$^7$ and 4f$^{14}$-shells) and occur as $Eu^{2+}$/$Eu^{3+}$ and $Yb^{2+}$/$Yb^{3+}$, respectively. In addition to the above mentioned arguments, the question arises whether the rare-earth atoms in EuAl$_2$X$_2$ and YbAl$_2$X$_2$ are di- or trivalent. A good probe for this is the magnetism of the 4f-shell: $Eu^{2+}$ has a magnetic moment of 7.94 $\mu_B$, $Eu^{3+}$ is nonmagnetic as $Yb^{2+}$ is, and $Yb^{3+}$ has a moment of 4.45 $\mu_B$. Magnetic measurements and a neutron diffraction experiment with EuAl$_2$Si$_2$ resulted considerably rescued magnetic moments for Eu about 7 $\mu_B$ in these compounds, which indicates intermediate valance. In this paper, the single-crystal structures of EuAl$_2$X$_2$ and YbAl$_2$X$_2$.The crystal structure of YbAl$_2$Si$_2$ was recently reported by us [2], YbAl$_2$Ge$_2$ was characterized only by powder data so far [3]. In this paper b, we report the single-crystal structures of EuAl$_2$X$_2$ and YbAl$_2$X$_2$, electrical conductivity and magnetic measurements are reported.

2. Experimental

All compounds were synthesized by direct reaction of the elements in corundum Crucibles at a temperature between is 1020 and1170 K. in quartz glass tubes under dry argon atmosphere. The first inhomogeneous products were homogenized in an argon-filled glove box and annealed twice at temperature between 1170 and 1270 K for 50 h. The resulting gray powders deteriorate slowly when exposed to; single crystals show metallic luster. Single-crystal data of EuAl$_2$Si$_2$, EuAl$_2$SGe$_2$, EuAl$_2$Si$_2$ and YbAl$_2$Ge$_2$ were collected with an automated four-circle diffractometer STOE AED-2 (Mo-Ka1, graphite monochromator, $\omega/\theta$-scan, $3^\circ < 2q < 80^\circ$). Absorption effects were collected by acquiring $\Psi$–$\omega$ scan data, structure refinements were performed with the SHELXL-97 [5] package. Electrical conductivities of all compounds were measured polycrystalline pellets using a four-probe dc current reversal technique between 8 and 300 K. The magnetic susceptibility of polycrystalline piece of LnAl$_2$X$_2$ compounds was measured with a SQUID Magnetometer between 2 and 300 K with magnetic flux densities up to 5.5 T. Self-consistent band structure calculations were performed using the LMTO method in its scalar relativistic version (program LMTO-ASA47) [1]. The basis sets consisted of 6s, 5d, 4f orbital for Eu/Yb, 3s, 3p for Si/Al and 4s, 4p for Ge. The 6p orbitals for Eu/Yb, 3d for Si/Al and 4d for Ge were treated by the downfolding technique [2]. To achieve space filling within the atomic sphere approximation, interstitial spheres are introduced to avoid too large overlap of the atom-centered spheres. The empty sphere positions and radii were calculated using an automatic procedure developed by Krier et al. [3]. Owing to the magnetic properties of the 4f-shell, spin-polarized calculations were performed using the exchange-correlation
3. Results and discussion

3.1 Structure refinements

Refinements of the single-crystal data EuAl$_2$Si$_2$, EuAl$_2$Ge$_2$, and YbAl$_2$Ge$_2$ converged rapidly with the atomic positions of CaAl$_2$Si$_2$ (space group P3m1) as starting parameters [1]. The results are summarized in the table below (Figure 1). In CaAl$_2$Si$_2$-type, the Si(Ge) atoms form a slightly distorted hexagonal close packing with Al occupying half the tetrahedral and the Ln (Ln=Yb,Eu) atoms half the octahedral voids. With regard to the Al-Si(Ge) bond distances, a main feature of the structure is a double layer of puckered AlSi(G) hexagons as shown in Figure 2. Herein the Al atoms are coordinated tetrahedrally by Si(Ge), which is itself surrounded umbrella-like by four Al atoms. The rare-earth atoms are located on hexagonal prisms build of six Si(Ge). Due to the puckering of the AlSi(Ge) hexagons, the Ln-Al distances are longer compared with the Ln-Si(Ge). The latter ones correspond to the sums of the atomic radii of Ln and the covalent radii for Si(Ge) for all compounds except YbAl$_2$Si$_2$ with slightly smaller Yb-Si bond lengths (-3.4%). This may be a hint for an intermediate valence state of Yb because the radius for Yb$^{3+}$ is smaller than for Yb$^{2+}$.

The ratio between the length of the Al-Si(Ge) bonds within and between the AlSi(Ge) hexagons indicates that EuAl$_2$Ge$_2$, compounds are CaAl$_2$Si$_2$-type structure. The structure refinements measurement give the value of 0.959, 0.967, 0.964 and 0.962 for YbAl$_2$Ge$_2$, EuAl$_2$Ge$_2$, EuAl$_2$Si$_2$ and YbAl$_2$Si$_2$ respectively [1]. From this all compounds described here are expected to contain divalent rare-earth atoms.

<table>
<thead>
<tr>
<th>Compound</th>
<th>YbAl$_2$Ge$_2$</th>
<th>EuAl$_2$Ge$_2$</th>
<th>EuAl$_2$Si$_2$</th>
</tr>
</thead>
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<tr>
<td>Space group</td>
<td>P3m1 (No. 164)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice parameters ($\AA$)</td>
<td>$a = 4.179(2)$, $c = 7.069(3)$</td>
<td>$a = 4.214(1)$, $c = 7.320(1)$</td>
<td>$a = 4.181(1)$, $c = 7.259(1)$</td>
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<tr>
<td>Volume ($\AA^3$)</td>
<td>106.9</td>
<td>112.57</td>
<td>109.89</td>
</tr>
<tr>
<td>Formula units per cell</td>
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<td></td>
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<tr>
<td>Calculated density ($g , cm^{-3}$)</td>
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<td>5.18</td>
<td>3.96</td>
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<td>$2\theta$ Range for data collection (°)</td>
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<tr>
<td>Total no. reflections</td>
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<td>1362</td>
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<tr>
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<tr>
<td>Absorption correction</td>
<td>ψ-scan</td>
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<td></td>
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<tr>
<td>Final $R_1$ indices ($I&gt;2\sigma(I)$)</td>
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<td>0.014</td>
<td>0.010</td>
</tr>
<tr>
<td>$wR_2$ (all data)</td>
<td>0.050</td>
<td>0.022</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Figure 1: Crystallographic data [1]
3.2 Magnetic and electrical properties

The temperature dependence of the inverse magnetic susceptibilities (1T measurements) of $\text{EuAl}_2\text{Si}_2$ and $\text{EuAl}_2\text{Ge}_2$ are shown in Figure 3. Above 80 K the susceptibilities $\text{EuAl}_2\text{Si}_2$ obeys modified Curie-Weiss law $\chi = \chi_0 + c/(T - \Theta)$. The data is fitted above 80 K with modified Curie-Weiss resulting in a paramagnetic Curie temperature (Weiss constant) of 23 K, magnetic moment of 7.82 $\mu_\beta$/Eu and a temperature independent contribution of $\chi_0 = 14 \times 10^{-9} m^3/mol$. The temperature independent contribution is in the order of magnitude of Pauli paramagnet and most likely results from the conduction of this metallic compound [1].
The 1/\( \chi \) versus T plot of EuAl\(_2\)Ge\(_2\) is almost linear. An evaluation of the data above 50 K according to the Curie-Weiss law resulted in an experimental magnetic moment of 7.90 \( \mu_\beta/\text{Eu} \) and a Weiss constant of 23 K. At low external magnetic fields (0.002 T) antiferromagnetic ordering is detected at \( T_N = 35.5 \) K for EuAl\(_2\)Si\(_2\) and at \( T_N = 27.5 \) K for EuAl\(_2\)Ge\(_2\) in perfect agreement with the previous study [2]. The magnetization behavior of EuAl\(_2\)Si\(_2\) and EuAl\(_2\)Ge\(_2\) is presented in Figure 4. At 50 K, well above the Néel temperature, the magnetization curves are almost linear as expected for a paramagnetic compound. At 4 K the magnetization of EuAl\(_2\)Si\(_2\) increases in a linear madder up to a critical field of B=1.3950 T and then shows a weaker increase. This may be ascribed to a metamagnetic (antiparallel to parallel spin alignment) or spin-flip transition. At the highest field strength about B=5.5 T the magnetization reached a value of 6.0 \( \mu_\beta/\text{Eu} \) at 4 K, comparable to the theoretical saturation magnetization of 7.0 \( \mu_\beta/\text{Eu} \). The magnetization behavior of EuAl\(_2\)Ge\(_2\) is quite similar with that of EuAl\(_2\)Si\(_2\).

The temperature dependence of inverse magnetic susceptibility of YbAl\(_2\)Si\(_2\) is shown in Figure 3. Between 100 and 300 K the 1/\( \chi \) versus T plot is almost linear. In this temperature region, an experimental magnetic moment of \( \mu_{\text{exp}} = 2.57 \mu_\beta/\text{Yb} \) can be determined according to the Curie-Weiss law \( \chi = c/(T-\Theta) \). The corresponding paramagnetic Curie temperature of 382 K is strongly negative as the frequency observed for intermediate-valent compounds [5]. In view of single crystallographic ytterbium site, YbAl\(_2\)Si\(_2\) may be classified as a homogeneously intermediate-valent compound.

The susceptibility versus temperature dependence of YbAl\(_2\)Ge\(_2\) is presented in the lower part of Figure 3. Down to about 80 K the susceptibility is almost temperature independent with a room temperature value of 1.2\( \times 10^{-9} \) m\(^3\)mol\(^{-1}\), compatible with Pauli paramagnetism [?]. The temperature dependencies of the electrical resistivities of LnAl\(_2\)X\(_2\) compounds are shown in Figure 5. The value is normalized to the resistivity at 300 K. All samples showed very low resistivities (about 0.2-1.2 m\( \Omega \)) and metallic behavior between 8 and 320 K. The peaks at 35 K for EuAl\(_2\)Si\(_2\) and 27 K for EuAl\(_2\)Ge\(_2\) coincide exactly with Neel temperatures determined by the SQUID experiments. Both ytterbium compounds show almost identical resistivities.
Figure 5: Temperature dependence of resistivity of compounds[1]

4. Conclusions

Crystallographic data and magnetic susceptibility measurement shows that LnAl$_2$X$_2$ compounds crystallize in the CaAl$_2$Si$_2$ type structure. All LnAl$_2$X$_2$ compounds are observed to be conductor between 8 and 320 K. Since they have small band gap, conduction is due to the metallic element in the compound.

References