Structure, exchange interactions and magnetic phase transition of Er2Fe17-xAlx intermetallic compounds

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Structure, exchange interactions, and magnetic phase transition of Er$_2$Fe$_{17-x}$Al$_x$ intermetallic compounds

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We present the effect of aluminum substitution on the structure, exchange interactions, and magnetic phase transitions of the intermetallic compound Er$_2$Fe$_{17}$. All samples have a hexagonal Th$_2$Ni$_17$-type structure or a rhombohedral Th$_2$Zn$_17$-type structure. The replacement of Fe by Al results in an approximately linear increase in the unit-cell volumes at a rate of 9.3 Å$^3$ per Al atom. The Al atoms preferentially occupy 12$d$ (18$h$) and 12$j$ (18$f$) sites at low Al concentration, while they prefer strongly to occupy 6$c$ (4$f$) and 18$j$ (12$j$) sites at high aluminum concentration. The Curie temperature is found to increase at first, form a maximum value at $x=3$, and then to decrease monotonically with increasing Al concentration. The exchange-coupling constant between 3$d$ and 4$f$ sublattices, $J_{RT}$, was obtained from fitting $M-T$ curves for some of the samples. The intersublattice molecular-field coefficient $n_{RT}$ and hence the $R-T$ exchange-coupling constant $J_{RT}$ have been also determined on the basis of magnetization curves at the compensation temperature. The exchange-coupling constant $J_{RT}$ shows almost no obvious composition dependence, while the exchange-coupling constant $J_{TT}$ is strongly dependent on the Al concentration. The composition dependence of the 3$d$ sublattice exchange interaction is discussed in terms of bond lengths and atomic preferential occupancies. It is noteworthy that the substitution of Al has a significant effect on the magnetocrystalline anisotropies of both the Er sublattice and the Fe sublattice in Er$_3$Fe$_{17-x}$Al$_x$ compounds. The temperature and composition dependence of the easy magnetization direction suggests that the second-order crystal electric-field coefficient $A_{20}$ changes its sign from negative to positive with increasing Al concentration up to $x>7$. [S0163-1829(98)02721-0]

I. INTRODUCTION

In the search for iron-rich new permanent magnet materials, the discovery of $R_2$Fe$_{17}$-(C, N, H)$_x$ ($R$ = rare-earth elements) obtained by the gas-solid reaction method has attracted considerable research activity. Sm$_2$Fe$_{17}$-(C, N)$_x$ is a very promising candidate as a permanent-magnet material. In order to overcome the drawback of its poor thermal stability, which restricts its practical application as a sintered magnet, Shen and co-workers found that the substitution of Ga, Al, or Si for Fe in Sm$_2$Fe$_{17}$C$_x$ can stabilize the high-carbon rare-earth compounds with 2:17-type structure. The arc-melted carbides are found to retain the 2:17 structure even at temperature above 1200 °C. Shen and co-workers have prepared single-phase $R_2$Fe$_{17-x}$Ga$_x$C$_2$ compounds by arc melting and found that the Curie temperature increases initially and then decreases with Ga substitution while $M_s$ decreases monotonically. These compounds have anisotropy fields exceeding 12 T. Cheng and co-workers found a similar behavior in Sm$_2$Fe$_{17-x}$Al$_x$C$_x$ where the $x=2$ compound has an anisotropy field of 11 T. The increase in Curie temperature with Al, Ga, and C has been attributed to the expansion of Fe-Fe bonds that compensates more for the dilution of the Fe sublattice. The high-temperature stability of the arc-melted carbides indicates that carbon is more strongly bonded than nitrogen in the samples formed by gas-solid reaction. These arc-melted carbides can be used as raw materials of high-performance sintered permanent magnets due to their high Curie temperature, strongly uniaxial anisotropy, as well as high-temperature stability.

Magnetocrystalline anisotropy and Curie temperature are the fundamental intrinsic magnetic parameters of permanent magnets and attract ever-growing attention from both experimentalsists and theoreticians. Large values of the uniaxial magnetocrystalline anisotropy are required to achieve high coercivities, and high Curie temperature can guarantee the magnets to have low-temperature coefficients of the hard magnetic properties so that they can be applied over a wide temperature range. The facts that all $R_2$Fe$_{17}$ binary compounds have low Curie temperatures and exhibit easy-plane anisotropy restrict their possible application as permanent magnets. Recently, it was found that the substitution of Ga, Al, or Si could not only facilitate the formation of $R_2$Fe$_{17}$ carbides with high carbon concentration, but also increase significantly the Curie temperature. Furthermore, the easy magnetization direction (EMD) of $R_2$Fe$_{17-x}M_x$ ($M$ = Ga or Al) alloys can be modified by the introduction of $M$ atoms. Low concentrations of Ga or Al substitution in
Sm$_2$Fe$_{17}$ results in a change in EMD from basal plane to $c$ axis without the presence of interstitial N or C atoms, while further substitution leads to a change from $c$ axis to plane again. A reversal change in EMD has been found in $R_x$Fe$_{17}$Ga$_y$ with $R$ = Tb, Dy, Ho, Er, Tm. The Fe sublattice can also exhibit uniaxial anisotropy at room temperature when the Ga concentration is very high ($x \approx 7$). The change in EMD implies that the crystal electric field (CEF) coefficients at the site $R$ are significantly influenced by the substituted atoms and this is worth more detailed investigation.

Knowing the intrinsic magnetic properties of the $R_x$Fe$_{17}$-$M_x$ ($M$ = Ga or Al) series is the first step in understanding the basic magnetic properties of the interstitial compounds derived from them. From the application point of view, these series are not very promising. However, from a fundamental point of view, they provide a very good opportunity to investigate the exchange interactions and anisotropies of the 3$d$ and 4$f$ sublattices because Al or Ga atoms can substitute for Fe atoms up to a very high concentration without changing the crystal structure, except for the unit-cell volume expansion. In this paper, the site occupancies of substituted atoms, exchange interactions between 3$d$ and 4$f$ sublattices, and the magnetocrystalline anisotropies of 3$d$ and 4$f$ sublattices in Er$_2$Fe$_{17}$-$Al_x$ compounds have been investigated by means of magnetization and ac susceptibility measurements, x-ray diffraction (XRD), and neutron diffraction (ND). The reason for selecting $R$ = Er is twofold. First, in the case of the Er$_2$Fe$_{17}$ compound, the Fe sublattice exhibits planar anisotropy, while the Er-sublattice anisotropy is expected to be uniaxial on the basis of the CEF effect in $R_x$Fe$_{17}$ compounds. Therefore, spin reorientations may occur in Er$_2$Fe$_{17}$-$Al_x$, either due to the temperature-induced competition between the Er and Fe sublattice anisotropies or due to the temperature-induced changes in the Er sublattice only. Second, the antiferromagnetic coupling between Er and Fe atoms allows us to investigate the intersublattice molecular-field coefficient $n_{RT}$ by means of the magnetization curves of Er$_2$Fe$_{17}$-$Al_x$ compounds at the compensation temperature. The temperature and composition dependence of magnetocrystalline anisotropy are explained in terms of a sign reversal of the second-order CEF coefficient $A_{20}$ from negative to positive when the Al concentration increases up to $x > 7$.

II. EXPERIMENTAL DETAILS

The samples of Er$_2$Fe$_{17}$-$Al_x$ $(0 \leq x \leq 9)$ were prepared by arc melting in an argon atmosphere of high purity. The elements used were at least 99.9% pure. An excess of 5% Er was added to compensate for the evaporation loss during melting. In order to ensure good homogeneity, the ingots were remelted at least four times, then annealed under an argon atmosphere at 1400 K for 5 days, followed by quenching into water. The ingots were ground to yield powders. The magnetic powders were oriented in an applied field of 1 T and fixed by means of epoxy resin to investigate the magnetocrystalline anisotropy.

The structural properties were investigated by means of XRD and ND. XRD experiments were performed on powder samples using Cu $K\alpha$ radiation to determine the crystal structure, lattice constants, and unit-cell volume. The powder ND experiments were employed to investigate the crystal structure, the occupancies of substituted atoms, as well as the magnetic structure.

The powder ND patterns of Er$_2$Fe$_{15}$Al$_2$ and Er$_2$Fe$_{12}$Al$_5$ were collected on a triple-axis spectrometer at China Institute of Atomic Energy at room temperature, while the pattern of Y$_2$Fe$_9$Al$_6$ was collected at 10 K to investigate the Fe sublattice anisotropy. The diffraction data were analyzed by Izumi’s Rietveld structure refinement program Rietan.$^{12}$

The magnetization curves were measured by using an extracting sample magnetometer with a magnetic field ranging from 0 to 6.5 T. The saturation magnetization was obtained from fitting the experimental data of $M(B)$ vs $B$ using the law of approach to saturation. The values of the Curie temperature were derived from the temperature dependence of magnetization $M(T)$ curves measured in a field of 0.05 T or ac susceptibility measured by an ac susceptibility magnetometer in a weak field of less than 0.0001 T at a frequency of 220 Hz.

III. RESULTS AND DISCUSSIONS

A. Structural properties

XRD patterns indicate that all samples are almost single phase with a hexagonal Th$_2$Ni$_{17}$-type structure or a rhombohedral Th$_2$Zn$_{17}$-type structure. The samples with low Al concentration crystallize in the hexagonal Th$_2$Ni$_{17}$-type structure, while those with high Al concentration crystallize in the rhombohedral Th$_2$Zn$_{17}$-type structure. The lattice constants $a$, $c$ and the unit-cell volume $v$ are summarized in Table I. In order to compare the volumes of the hexagonal cell with the rhombohedral one, we have multiplied the former by a factor of $\frac{2}{3}$. It can be found that the substitution of larger Al atoms for Fe atoms leads to an approximately linear increase in the unit-cell volumes at a rate of 9.3 Å$^3$ per Al atom.

The atomic occupancies were investigated by means of ND pattern on the powder samples of Er$_2$Fe$_{15}$Al$_2$ and Er$_2$Fe$_{12}$Al$_5$ at room temperature and Y$_2$Fe$_9$Al$_6$ at 10 K. For example, the ND patterns of Er$_2$Fe$_{15}$Al$_2$ and Er$_2$Fe$_{12}$Al$_5$ are shown in Fig. 1. The crystallographic parameters of the Th$_2$Ni$_{17}$ or Th$_2$Zn$_{17}$-type $R$-Fe compounds were used to start the refinement. The rhombohedral compound has only one crystallographically nonequivalent $R$ site ($6c$), while the hexagonal compound has two crystallographically nonequivalent $R$ sites ($2b$ and $2d$). These sites are, however, characterized by a quite similar local atomic arrangement of Fe atoms and a slightly different arrangement of the $R$ atoms. The hexagonal 4$f$, 6$g$, 12$f$, and 12$k$ sites correspond to the rhombohedral 6$c$, 9$d$, 18$f$, and 18$h$ sites, respectively. Initially, it was assumed that the Al and Fe atoms occupy the four nonequivalent sites statistically. According to the chemical concentration and with the linear constraint condition, the sum of the fractional occupancies of Fe and Al atoms on each of these four sites was fixed to be equal to 1.0. The initial magnetic moments were taken equal to 2.0$\mu_B$, $-1.0\mu_B$, and 0.0$\mu_B$ for Fe, Er, and Y atoms, respectively, and all magnetic moments being in a parallel arrangement in a plane perpendicular to the sixfold axes. Refined values of the lattice and positional parameters, atomic occupancies, and magnetic moments of Er$_2$Fe$_{15}$Al$_2$ and Er$_2$Fe$_{12}$Al$_5$ at room
The magnetic moments of Er and Fe are antiferromagnetically coupled. It is noteworthy that the Fe magnetic moments are along ferromagnetically coupled. The magnetic moments orientation will be discussed in detail in the following section. The Rietveld structure analyses show an obvious concentration dependence fractional occupancy of Al on each of the four crystallographic sites, 6c(4f), 9d(6g), 18f(12j), and 18h(12k), in $R_2\text{Fe}_{17-x}\text{Al}_x$ (Fig. 2). For comparison, the results that would be expected for a random substitution of Al on the Fe sites are also presented in Fig. 2. It can be seen from Fig. 2 that the Al atoms prefer 18f(12j) and 18h(12k) sites at low Al concentration, whereas they prefer strongly to occupy 6c(4f) and 18f(12j) sites at high Al concentration. The 6c(4f) site initially does not take up aluminum, but at high Al content up to 80% of this site is occupied by Al atoms for $Y_2\text{Fe}_9\text{Al}_8$. The 9d(6g) site excludes Al at all concentrations. The Al fractional occupancies at the 18f(12j) site increase monotonically, but those at the 18h(12k) site become saturated at about 40%. This result is very similar to that of Nd$_2\text{Fe}_{17-x}\text{Al}_x$. The atomic preferential occupancies are determined to a large extent by the Wigner-Seitz cell volume. Because Al atoms have larger metallic radii than iron, they prefer to occupy the 6c(4f) site which has, especially in higher aluminum concentration, the largest Wigner-Seitz cell volume, and avoid occupying the 9d(6g) site that has the smallest Wigner-Seitz cell volume. If a site is unoccupied by Al, its near neighbors prefer to accept Al atoms. Thus, because the 9d(6g) site has four 18f(12j) and four 18h(12k) sites as near neighbors, these latter sites are in favor of accepting Al atoms.

### B. Saturation magnetization and magnetic moments

Figure 3 shows the magnetization curves of $R_2\text{Fe}_{17-x}\text{Al}_x$ compounds measured at 1.5 K. It is found that the saturation magnetization decreases linearly with increasing Al concentration, and this decrease is much faster than in the case of a simple magnetic dilution as shown by the dotted line in Fig. 4. This implies that the decrease in saturation magnetization is not only due to the simple magnetic dilution, but also due to the decrease of Fe magnetic moments. The antiparallel coupling between the $R$ spin moment and the Fe moment leads to ferrimagnetism for the heavy rare-earth compounds.
TABLE II. Crystallographic and magnetic parameters of Er$_2$Fe$_{15}$Al$_2$ and Er$_2$Fe$_{12}$Al$_5$ at room temperature and Y$_2$Fe$_9$Al$_8$ at 10 K.

<table>
<thead>
<tr>
<th>Atom site</th>
<th>Occupancy</th>
<th>$x$ $y$ $z$</th>
<th>$M(\mu_B)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$<em>2$Fe$</em>{15}$Al$_2$</td>
<td>$P_{63}/mmc$</td>
<td>$a=b=8.521(1)$ Å</td>
<td>$c=8.335(8)$ Å</td>
</tr>
<tr>
<td>Er(2b)</td>
<td>1.00</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Er(2d)</td>
<td>1.00</td>
<td>0.333(3)</td>
<td>0.666(7)</td>
</tr>
<tr>
<td>Fe(4f)</td>
<td>1.00</td>
<td>0.333(3)</td>
<td>0.666(7)</td>
</tr>
<tr>
<td>Fe(6g)</td>
<td>1.00</td>
<td>0.500</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(12j)</td>
<td>0.79</td>
<td>0.330(1)</td>
<td>-0.041(1)</td>
</tr>
<tr>
<td>Fe(12k)</td>
<td>0.87</td>
<td>0.165(1)</td>
<td>0.330(1)</td>
</tr>
<tr>
<td>Al(12j)</td>
<td>0.21</td>
<td>0.330(1)</td>
<td>-0.041(1)</td>
</tr>
<tr>
<td>Al(12k)</td>
<td>0.13</td>
<td>0.165(1)</td>
<td>0.330(1)</td>
</tr>
<tr>
<td>Er$<em>2$Fe$</em>{12}$Al$_5$</td>
<td>$R\bar{3}m$</td>
<td>$a=b=8.645(2)$ Å</td>
<td>$c=12.648(3)$ Å</td>
</tr>
<tr>
<td>Er(6c)</td>
<td>1.00</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(6c)</td>
<td>0.63</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(9d)</td>
<td>1.00</td>
<td>0.500</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(18f)</td>
<td>0.65</td>
<td>0.295(1)</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(18h)</td>
<td>0.64</td>
<td>0.502(1)</td>
<td>0.498(1)</td>
</tr>
<tr>
<td>Al(6c)</td>
<td>0.37</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Al(18f)</td>
<td>0.35</td>
<td>0.295(1)</td>
<td>0.000</td>
</tr>
<tr>
<td>Al(18h)</td>
<td>0.36</td>
<td>0.502(1)</td>
<td>0.498(1)</td>
</tr>
<tr>
<td>Y$_2$Fe$_9$Al$_8$</td>
<td>$R\bar{3}m$</td>
<td>$a=b=8.7446(6)$ Å</td>
<td>$c=12.6728(1)$ Å</td>
</tr>
<tr>
<td>Y(6c)</td>
<td>1.00</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(6c)</td>
<td>0.20(1)</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(9d)</td>
<td>1.00</td>
<td>0.500</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(18f)</td>
<td>0.29(1)</td>
<td>0.290(5)</td>
<td>0.000</td>
</tr>
<tr>
<td>Fe(18h)</td>
<td>0.60(1)</td>
<td>0.501(5)</td>
<td>0.498(5)</td>
</tr>
<tr>
<td>Al(6c)</td>
<td>0.80(1)</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>Al(18f)</td>
<td>0.71(1)</td>
<td>0.290(5)</td>
<td>0.000</td>
</tr>
<tr>
<td>Al(18h)</td>
<td>0.40</td>
<td>0.501(5)</td>
<td>0.498(5)</td>
</tr>
</tbody>
</table>

$^a$The magnetic moments are oriented along [h00] at room temperature.

$^b$The magnetic moments are oriented along [001] at 10 K.

Accordingly, the saturation moments of Er$_2$Fe$_{17-x}$Al$_x$ compounds can be expressed by the equation

$$M_S = M_T - M_R = (17-x) \mu_{Fe} - 2 \mu_{Er},$$  

(1)

where $M_T$ is the magnetic moment of the $T=$(Fe, Al) sublattice and $M_R$ is the moment of the Er sublattice.

If we assume the Er magnetic moment is equal to the free-ion magnetic moment $\mu_{Er} = 9.0 \mu_B$, the average Fe mag-

FIG. 2. Concentration dependence of the fractional occupancy on each of the four crystallographic sites [6c(4f), 9d(6g), 18f(12j), and 18h(12k)] in $R_2$Fe$_{17-x}$Al$_x$ (R=Er or Y). The dashed line represents the random substitution model.

FIG. 3. Magnetization curves of Er$_2$Fe$_{17-x}$Al$_x$ compounds at 1.5 K.
In order to avoid the effect of a strong magnetic moments of Er\textsubscript{2}Fe\textsubscript{17} can be obtained. They are found to decrease with increasing Al concentration (Table I).

With increasing Al concentration, the T-sublattice moment will decrease. For the sample with x=6, it is about equal to the Er sublattice moment at 1.5 K. The T-sublattice moments will be lower than the Er sublattice and therefore a negative value of the magnetic moment of Er\textsubscript{2}Fe\textsubscript{17} can be obtained. They are found to decrease with increasing Al concentration (Table I).

The concentration dependence of the Curie temperature $T_c$ and the compensation temperature $T_{comp}$ of Er\textsubscript{2}Fe\textsubscript{17-x}Al\textsubscript{x} are illustrated in Fig. 6. A small substitution of Al results in an enhancement of the Curie temperature from 297 K for x=0 to 407 K for x=3. Further substitution leads to a decrease in Curie temperature. The initial increase in Curie temperature is a common feature in intermetallic compounds. The Curie temperatures of R-T intermetallics are determined by the three different exchange-coupling constants: $J_{RT}$, $J_{RR}$, and $J_{TT}$. $J_{RT}$ primarily governs the temperature dependence of the 3d moment and the Curie temperature $T_c$. The 3d-4f interaction $J_{RT}$ has only a minor influence on the Curie temperature, especially for compounds rich in iron, such as R\textsubscript{2}Fe\textsubscript{17}, R\textsubscript{2}Fe\textsubscript{14}B, and R(Fe,M)\textsubscript{12}. However, it dominates the molecular field experienced by the rare-earth moment that, in turn, determines the temperature dependence of the magnetic moment and the magnetocrystalline anisotropy of the rare-earth ions. The R-R interaction is generally neglected because it is smaller than the T-T and R-T interaction. In addition, there are few R-R bonds in the Fe-rich compounds. Thus, the standard molecular-field expression of the Curie temperature for two-sublattice R-T compounds can be written as

$$3kT_c = a_{TT} + [a_{TT}^2 + 4a_{RT}a_{TR}]^{1/2},$$

where $a_{TT} = Z_{TT}J_{TT}S_f(S_f+1)$ and

$$a_{RT}a_{TR} = Z_{RT}Z_{TR}S_f(S_f+1)(g_R-1)^2J_R(J_R+1)J_{RT},$$

where $S_f$, $J_R$ are the spin moment and total moment of T and R ions, respectively, $g_R$ is the Landé g factor of the R ions. $Z_{ij}$ (i=R, j=T, or i=T, j=R) is the number of j

FIG. 4. Saturation magnetization of Er\textsubscript{2}Fe\textsubscript{17-x}Al\textsubscript{x} compounds at 1.5 K as a function of aluminum concentration. The dotted line represents the magnetization for simple magnetic dilution model.
neighbors to an \( i \) atom, \( Z_{TT} \) is the number of \( T \) neighbors to a given \( T \) atom. The value of \( Z_{RT} \) is related to \( Z_{TR} \) via the relation \( N_R Z_{RT} = N_T Z_{TR} \). The values of \( J_{RT} \) are obtained either by high-field magnetization measurements on free powder particles of polycrystalline samples or by comparison of the difference in Curie temperatures for compounds with \( M_R = 0 \) ( \( a_{RT} = a_{TR} = 0 \) ) such as \( R = Y \), La, and Lu. \( J_{RT} \) can be obtained either by high-field magnetization measurements on free powder particles of polycrystalline samples or by comparison of the difference in Curie temperatures for compounds with \( M_R = 0 \) ( \( T_T = T_{c0} \)) and \( M_T = 0 \) ( \( T_R = T_{c0} \)) such as \( R = Y \), La, Lu, using the high-temperature approximation of the molecular-field model:

\[
J_{RT}^2 = 9k_B^2T_{c,R}(T_{c,R} - T_{c0}^2)/4Z_{RT}Z_{TR}S_T(S_T + 1)
\times (g_R - 1)^2 J_R(J_R + 1).
\]  

In the first model, very high magnetic fields are required. Because the magnetic field available to many laboratories is limited, it is difficult to determine \( J_{RT} \) precisely in many cases. The second method is generally used under the assumption that \( J_{RT} \) is constant regardless of which \( R \) element is considered in \( R_xFe_{1-x}Al_x \). Problems in applying Eq. (3) may arise when the \( T-T \) interaction varies across the \( R \) series, since \( J_{RT} \) may depend strongly on the interatomic distance between the nearest-neighbor magnetic atoms. The lattice constants of \( R_xFe_{1-x} \), and consequently, the interatomic distance of Fe-Fe pairs, are not the same for different \( R \) elements considered here (Er and Y). Therefore, the assumption of the same value of \( J_{RT} \) among in these series is not realistic. In this work, we will determine \( J_{RT} \) and \( J_{TT} \) on the basis of the molecular-field model by fitting the temperature dependence of the magnetization.

Figure 7 presents several \( M-T \) curves calculated for the \( Er_xFe_{1-x}Al_x \) compounds with \( x = 7 \) to 9 by using the molecular-field expressions. In fitting the \( M-T \) curves, the exchange-coupling constant obtained from the magnetization curves at the compensation temperature.

The exchange-coupling constant obtained from fitting the \( M-T \) curves.

Table III. The intersublattice molecular-field coefficient \( n_{RT} \), the critical magnetic field \( B_{crit,1} \), and \( B_{crit,2} \), the molecular field at Er ions \( b_{mol,Er} \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>( n_{Er} )</th>
<th>( B_{mol,Er} )</th>
<th>( B_{crit,1} )</th>
<th>( B_{crit,2} )</th>
<th>( J_{Er} / k_B )</th>
<th>( J_{Er} / k_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2.34</td>
<td>36.5</td>
<td>5.6</td>
<td>78.6</td>
<td>4.4</td>
<td>12.9</td>
</tr>
<tr>
<td>8</td>
<td>2.34</td>
<td>33.5</td>
<td>8.7</td>
<td>75.6</td>
<td>4.4</td>
<td>11.6</td>
</tr>
<tr>
<td>9</td>
<td>2.37</td>
<td>29.2</td>
<td>13.5</td>
<td>71.8</td>
<td>5.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>

aExchange-coupling constant obtained from the magnetization curves at the compensation temperature.
bExchange-coupling constant obtained from fitting the \( M-T \) curves.

At the compensation temperature \( M_R(T_{comp}) \), the linear range with \( M = B/n_{RT} \) starts at \( B = 0 \) T. Experimentally, the field dependence of the magnetization close to the compensation temperature was found to be linear at all but the lowest field strengths (Fig. 8). From the slope of the linear parts, we have determined the values of the intersublattice molecular-field coefficient \( n_{ET} \) at the compensation temperature. The Er-\( T \) exchange-coupling constant \( J_{ErT} \) can be directly obtained from the relation between \( J_{RT} \) and \( n_{RT} \). The results are tabulated in Table III where it can be seen that the values of \( J_{ErT} \) obtained by the two methods described above are of comparable magnitude.

The values of \( J_{ErT} \) show no obvious dependence on the Al concentration in \( Er_xFe_{1-x}Al_x \) compounds. This result is in good agreement with previous work. If we use the average value \( J_{ErT} / k_B = 10.1 \) K, the \( T-T \) exchange-coupling constant \( J_{TT} \) can be obtained from Eq. (2). The values of \( J_{TT} \) are listed in Table I and as a function of Al concentration are plotted in Fig. 6. It can be seen that the effect of \( R-T \) ex-
indicate that the initial Curie temperature enhancement in the mechanism of this enhancement in 

Due to the short 6c-6c bond length, the 6c site is generally believed to be responsible for the low Curie temperature of the R₂Fe₁₇ compounds. However, the ND results clearly indicate that the initial Curie temperature enhancement in R₂Fe₁₇₋ₓAlₓ compounds is not a result of the removal of iron 6c “dumbbell” atoms by substitution of Al onto these sites, but that it has to be attributed to the overall increase in Fe-Fe bond lengths, which overcompensates the dilution of Fe atoms, although magnetic dilution becomes more important in determining the Curie temperature upon further substitution of the nonmagnetic Al atoms. It is noteworthy that the value of Jₜₜ increases again at the highest Al concentrations. This phenomenon was also observed in other R₂Fe₁₇₋ₓGaₓ (R = Dy, Ho, Er, or Tm) compounds. Simultaneously, the ND results demonstrate that the Al atoms strongly prefer to occupy the 6c site. The increase in T-T exchange interaction is perhaps related to the preferential substitution of Al for Fe onto this site. An investigation of the mechanism of this enhancement in Jₜₜ, and hence, in Curie temperature is in progress.

D. Magnetocrystalline anisotropy and magnetic phase transition

In general, the overall magnetocrystalline anisotropy of R-T intermetallics is the sum of 4f-sublattice and 3d-sublattice anisotropies. In the case of R₂Fe₁₇ compounds

\[ K_{1,\text{tot}} = 2K_{1,R} + K_{1,\text{Fe}}, \]

where K₁,R is the contribution of one R³⁺ ion to the anisotropy constant and K₁,Fe is the anisotropy constant of the Fe sublattice. In the first approximation, K₁,R can be described as

\[ K_{1,R} = -\frac{3}{2} \alpha J A_{20}(r_s^2/(3J_{R,z}^2 - J_R(J_R + 1))), \]

where α is the second-order Stevens factor and A₂₀ is the second-order CEF coefficient.

In the case of Er₂Fe₁₇, the Fe sublattice exhibits an easy-plane anisotropy, i.e., K₁,Fe < 0, while the Er-sublattice anisotropy is dependent on the product of α₁ and A₁₀. For the Er³⁺ ion, α₁ > 0. Hence, a negative A₁₀ will make the Er-sublattice moments favor c-axis orientation at low temperature, K₁,Er > 0. Although there are two crystallographically distinct sites in Er₂Fe₁₇, it was proved that the CEF anisotropy can be described using a single set of crystal-field parameters averaged over the two sites. Values of +17.9K₁₀⁻² and −8.9K₁₀⁻⁴ for the second- and the fourth-order CEF coefficients A₁₀ and A₄₀ respectively, have been deduced by Andreev et al. from magnetization studies up to 6 T. According to these results, Er₂Fe₁₇ compound would not follow the systematic of the Stevens factor α₁ for the easy magnetization direction. In order to determine the CEF coefficients precisely, Garcia-Landa et al. investigated R₂Fe₁₇ single crystals (R = Y, Dy, Ho, and Er) by means of high-field magnetization in a magnetic field up to 51 T, and obtained the values of −24.58K₁₀⁻² and −11.88K₁₀⁻⁴ for A₁₀ and A₄₀ respectively. The value of the CEF coefficient A₁₀ is in agreement with the results of the Mössbauer effect in Er₂Fe₁₇, for which the average value A₁₀=−50 ± 100K₁₀⁻² was found. If we only take into account the second-order CEF term, a value of K₁,R = +7.0 K/f.u. can be derived on the basis of Eq. (8), which is compatible with the value of K₁,Er=8.5 K/f.u. obtained by Franse et al. Since its absolute value is much smaller and decreases more rapidly with increasing temperature than that of K₁,Er=50.4 K/f.u. (at 4.2 K), no spin reorientation is expected to occur when the temperature varies between cryogenic temperatures and the Curie temperature.

The value of the ac susceptibility χ’ of an intermetallic compound depends strongly on its magnetic anisotropy and domain-wall energy. It is proportional to M₂²/√AK₁ for domain-wall displacement or M₂²/K₁ for domain rotation. Both saturation magnetization Mₛ and anisotropy constant K₁ strongly vary with temperature; thus the shape of the χ’ vs T curve is strongly affected by the temperature dependence of Mₛ and K₁. At the spin-reorientation temperature, the change of Mₛ is relatively smooth, while K₁ changes drastically, which is reflected as a kink in the χ’ vs T curves. The spin-reorientation temperatures Tₛ can be taken as the temperatures at which the first deviation of the ac susceptibility dχ’/dT reaches an extreme value (maximum or minimum). Measurements of temperature dependence of the ac susceptibility can be therefore used to detect temperature-induced magnetic-phase transitions. Figure 9 shows the temperature dependence of the χ’ of Er₂Fe₁₇₋ₓAlₓ compounds with x = 1, 2, 3, and 4. An anomaly is visible for each of the samples. The anomalies in χ’ become more clear if dχ’/dT is plotted as a function of temperature, as shown in Fig. 10. Anomalies are also observed in the M-T curves measured at a low magnetic field of 0.05 T (Fig. 11). Considering the temperature-induced competition between the planar Fe-sublattice anisotropy and the uniaxial Er-sublattice anisotropy, one can attribute these anomalies to spin reorientations. The spin-reorientation temperatures are found to increase first, have a maximum value at x = 3, and then decrease. Similar results have also been observed in Er₂Fe₁₇₋ₓGaₓC₂ and Er₂Fe₁₇₋ₓSiₓ. For the samples with x = 5, 6, and 7,
no spin reorientation was detected from the temperature dependence of the ac susceptibility. The sharp peaks at the temperatures of 246 and 182 K for the samples with $x = 5$, 6, and 7, respectively, correspond to their Curie temperatures. These results suggest that the substitution of Al atoms has an effect not only on the Fe-sublattice anisotropy, but also on the Er-sublattice anisotropy.

In order to determine the contributions of these two sublattices to the overall anisotropy separately, one can choose the $R$ elements without contribution to the $R$-sublattice anisotropy in $R_2Fe_{17-x}Al_x$. Thus, at first we studied the Fe-sublattice anisotropy by selecting $R = Y$ or Gd. The planar anisotropy constants $K_{1,Fe}$ of $Y_2Fe_{17-x}Al_x$ compounds with $x < 6$ have been obtained from the magnetization measurements on the magnetically aligned powders on the basis of a simple theoretical model proposed by Li et al.\(^3\)\(^2\) They are weakened by Al substitution (Fig. 13). The nonlinear decrease of $K_{1,Fe}$ in absolute value implies that the fractional occupancies of Al atoms at the four nonequivalent sites are not the same and that the contributions of these four sites to the overall anisotropy are different.

Since the composition dependence of the Al and Ga atomic occupancies in $R_2Fe_{17-x}M_x$ ($M = Ga$ or $Al$) compounds is almost the same,\(^1\)\(^3\),\(^1\)\(^5\),\(^3\)\(^3\),\(^3\)\(^4\) one can expect on the basis of the results obtained for $R_2Fe_{17-x}Ga$ that the further introduction of Al atoms results in an easy $c$-axis anisotropy of the Fe sublattice. Because $Y_2Fe_{10}Al_7$ cannot be magnetically aligned at room temperature due to its low Curie temperature, we aligned Gd$_2$Fe$_{10}Al_7$ powders instead of $Y_2Fe_{10}Al_7$ to investigate the Fe-sublattice anisotropy. Easy $c$-axis anisotropy of the Fe sublattice was, however, not observed for $x < 7$, while for further increase in Al concentration the Curie temperature was lower than room temperature. Because of its capability of investigating microscopically the crystal and magnetic structure, ND study on $Y_2Fe_{9}Al_8$ has been undertaken at low temperature to determine the magnetic moment orientation. The refinement results, as summarized in Table II, indicate that the Fe moments are oriented...
along [001]. This means that a uniaxial anisotropy of the Fe sublattice can be induced also by the introduction of Al atoms. Comparing the occupancies of Al atoms with those of Ga atoms, one can deduce that the Al or Ga atoms preferentially occupy 6c and 18f sites, which may make a predominant contribution to the easy-plane anisotropy. When the Fe atoms at these sites are replaced by nonmagnetic atoms, a positive $K_{1,Fe}$ may be obtained, that is, a uniaxial anisotropy of the Fe sublattice can be induced. A detailed investigation of the contribution of the individual sites to the overall anisotropy will be undertaken in the near future.

As can be seen in Fig. 13, the absolute value of the anisotropy constant $K_1$ decreases from 50.4 K/f.u. for Y$_2$Fe$_{17}$ to 17.0 K/f.u. for Y$_2$Fe$_{15}$Al$_2$ at 4.2 K. In view of the fact that for the sample Er$_2$Fe$_{15}$Al$_2$, the easy magnetization direction changes from basal plane to $c$ axis with decreasing temperature, this suggests $K_{1,Er}$.

With decreasing temperature, no spin reorientation is found in the Er$_2$Fe$_{17}$-$x$Al$_x$ samples with $x = 5, 6, and 7$. This implies that there are two possibilities: (1) $K_{1,Er} > |K_{1,Fe}|$ or (2) $K_{1,Er} < |K_{1,Fe}|$ at all temperatures. The first possibility can be excluded on the basis of ND results that Er$_2$Fe$_{15}$Al$_5$ exhibits easy-plane anisotropy at room temperature. Thus, it is only possible that $K_{1,Er} < |K_{1,Fe}|$ for the compounds with $x = 5, 6, and 7$ at all temperatures. Thus, the value of $K_{1,Er}$ also decreases with further increasing Al concentration. The easy $c$-axis anisotropy of the Er sublattice is not strong enough to overcome the planar anisotropy of the Fe sublattice. The decrease of $K_{1,Er}$ is attributed to the $A_{20}$ decreases in negative value with increasing Al concentration. For example, for the compound with $x = 6$, $K_{1,Er} = -4.2$ K/f.u. at 4.2 K. This means that $K_{1,Er} < 4.2$ K/f.u. at 4.2 K. On the basis of Eq. (8), the absolute value of $A_{20}$ will reduce to less than $14.75 K a_0^{-2}$ for Er$_2$Fe$_{10}$Al$_6$.

The sharp peaks are attributed to the Curie temperatures, as are shown in Fig. 5, while the anomalies at low temperatures are related to spin reorientations. For the compounds with $x = 8$ and 9, the uniaxial Fe sublattice anisotropy dominates the overall magnetocrystalline anisotropy at high temperatures. Because the Er sublattice plays a more important role in determining the EMD at low temperature, it is reasonable to assume that the EMD changes from $c$ axis to basal plane with decreasing temperature in these two compounds. The magnetic phase diagram of Er$_2$Fe$_{17}$-$x$Al$_x$ compounds is illustrated in Fig. 15. The fact that the EMD changes from $c$ axis at high temperature to basal plane at low temperature implies that the sign of the second-order CEF coefficient $A_{20}$ has changed from negative to positive with increasing Al substitution for $x > 8$. A similar effect of Ga substitution on the CEF coefficient was also observed in Tb$_2$Fe$_{17}$-$x$Ga$_x$ compounds by neutron-diffraction studies.

Band-structure calculations have demonstrated that the second-order CEF coefficient $A_{20}$ is determined predomi-

![FIG. 13. Concentration dependence of the anisotropy constant $K_I$ and the anisotropy fields $\mu_0 H_A$ of Y$_2$Fe$_{17-x}$Al$_x$ compounds.](image1)

![FIG. 14. Temperature dependence of the ac susceptibility of Er$_2$Fe$_{17-x}$Al$_x$ with $x = 8$ and 9.](image2)

![FIG. 15. Magnetic-phase diagram of Er$_2$Fe$_{17-x}$Al$_x$ compounds.](image3)
nantly by the $R$ ions’ $5d$ and $6p$ valence-electron charge asphericity.\textsuperscript{35} It is strongly influenced by the variation of $x$ in $R_x$Fe$_{17-2x}$Al$_x$ because of the changing hybridization of the $R$ ions’ $5d$ and $6p$ valence-electron states with the valence-electron states of the neighbor atoms. Quite substantial changes in the magnitude and sign of the $R$ valence-electron asphericity can be expected when Al preferentially substitutes into the nearest-neighbor sites of the $R$ atoms.

### IV. CONCLUSION

On the basis of the correlation between the Al atom occupancies in Er$_x$Fe$_{17-2x}$Al$_x$ compounds and the Er- and $T$-sublattice anisotropies, it is reasonable to conclude the following. (1) The Fe atoms at 6$c$ (4$f$) and 18(12$j$) sites have a predominantly negative contribution to the anisotropy of Fe sublattice. When they are replaced by nonmagnetic Al atoms, a positive $K_{1,Fe}$, and hence, uniaxial anisotropy of the Fe sublattice may be obtained. (2) The preferential occupancies of the substituted atoms have a significant effect on the CEF coefficients at the Er site, and consequently, on the Er-sublattice anisotropy. The preferential occupancy of Al atoms at the 18$h$ site, which is the nearest-neighbor of the Er site in the $c$-axis direction (different layer) seems to make the $A_{20}$ values more negative, and hence to increase the uniaxial anisotropy of Er sublattice. Thus, a small degree of Al substitution can increase the spin-reorientation temperature of Er$_x$Fe$_{17-2x}$Al$_x$ compounds. The preferential occupancies of Al atoms into the 18$f$ site, which shares the Er site at the same basal plane, appears to make the $A_{20}$ values less negative, and finally lead to a sign reversal from negative to positive. Therefore, relatively high Al substitution in Er$_x$Fe$_{17-2x}$Al$_x$ will change the EMD of the Er-sublattice moments from $c$ axis to basal plane.

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