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MAGNETIC BEHAVIOUR OF THE CUBIC La(Fe,Al)\textsubscript{13} COMPOUNDS

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The magnetic properties of the cubic NaZn\textsubscript{13} type pseudobinary compounds LaFe\textsubscript{x}Al\textsubscript{13-x} were studied in the temperature range T=4.2 - 300 K by means of $^{57}$Fe-Mössbauer spectroscopy, magnetization and zero-field susceptibility measurements. The compounds LaFe\textsubscript{x}Al\textsubscript{13-x} show a rather peculiar concentration dependence of the type of magnetic ordering as well as of the ordering temperature.

1. Introduction

LaCO\textsubscript{13}, which is strongly ferromagnetic, is the only compound among 45 binary systems consisting of a rare earth element (R) and one of the metals Fe,Co or Ni (T) with the cubic NaZn\textsubscript{13} type of structure. Kripyakevich et al.\cite{1} showed that the cubic NaZn\textsubscript{13} type of structure can be stabilized in other binary rare earth transition metal systems (R-T) by substitution of Si for part of the transition metal T in RT\textsubscript{13}. Previously we have studied LaFe\textsubscript{x}Si\textsubscript{13-x} \cite{2} in the concentration region 10.5 ≤ x ≤ 11.5. Only in this region single phase samples were obtained. In the present investigation we show that the structure stabilization occurs over a much wider concentration range when part of the transition metal T is substituted by Al. We have studied the magnetic properties of LaFe\textsubscript{x}Al\textsubscript{13-x} by means of $^{57}$Fe-Mössbauer spectroscopy, magnetization and temperature-dependent zero-field susceptibility measurements.

2. Experimental

The samples of the compounds LaFe\textsubscript{x}Al\textsubscript{13-x} were prepared by argon arc melting of the appropriate amounts of the starting materials and vacuum annealed for about 10 days at T=1200 K. The samples were investigated by means of X-ray diffraction. Single phase samples of the cubic NaZn\textsubscript{13} type of structure were obtained in the concentration range 6 ≤ x < 12. For x < 6 a contamination with compounds of the tetragonal ThMn\textsubscript{12} structure is observed in the samples. Microscopic measurements indicate besides the NaZn\textsubscript{13} type of structure a so far unidentified second phase for x ≥ 12.

The magnetic properties of these samples were determined by means of an adapted Faraday method in the range T=4.2 - 300 K using magnetic field strengths up to 1.8 T. The temperature dependence of the zero-field susceptibility has been determined with a sensitive pendulum magnetometer in the same T-range.

The $^{57}$Fe-Mössbauer spectra were obtained by means of a standard constant-acceleration type spectrometer by using a $^{57}$Co-Rh source.

3. Results

The shape of the magnetization versus temperature curve for
The saturation moment per iron atom at $T=4.2$ K ($\mu_s$) and the values of the Curie temperature ($T_C$) are listed for the various compounds in Table 1 and plotted in fig. 1.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$ (Å)</th>
<th>$T_C$ (K)</th>
<th>$\mu_s$ (μB/Fe)</th>
<th>$T'_C$ (K)</th>
<th>$H_{eff}$ (T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>11.93</td>
<td>-</td>
<td>0</td>
<td>65</td>
<td>12.0</td>
</tr>
<tr>
<td>7</td>
<td>11.86</td>
<td>-</td>
<td>0</td>
<td>55</td>
<td>12.0</td>
</tr>
<tr>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>8</td>
<td>11.80</td>
<td>138</td>
<td>1.02</td>
<td>126</td>
<td>14.5</td>
</tr>
<tr>
<td>9</td>
<td>11.74</td>
<td>237</td>
<td>1.47</td>
<td>238</td>
<td>19.0</td>
</tr>
<tr>
<td>10</td>
<td>11.67</td>
<td>250</td>
<td>1.66</td>
<td>250</td>
<td>22.0</td>
</tr>
<tr>
<td>11</td>
<td>11.61</td>
<td>195</td>
<td>2.00</td>
<td>190</td>
<td>26.5</td>
</tr>
<tr>
<td>11.8</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12.0</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>235</td>
<td>26.0</td>
</tr>
</tbody>
</table>

The saturation moment increases from $\mu_s = 0$ μB for $x = 7$ to $\mu_s = 2.0$ μB for $x = 11$. For $x > 11$ the magnetization is strongly decreasing to about $\mu_s = 0.1$ μB/Fe for $x = 11.8$. However for $x = 12.0$ $\mu_s = 1$ μB/Fe is measured. The Curie temperature ($T_C$) determined from magnetization measurements increases with increasing $x$ and after reaching a maximum for $x = 9.5$ it decreases. For $x > 11$ it was impossible to determine $T_C$ in this way.

In fig. 2 we have plotted the temperature dependence of the zero-field susceptibility for $x = 11.2$, 11.5, 11.8 and 12.0 respectively. The shape of the curve as found for $x = 11.2$ is characteristic for $x < 11.2$, indicating a sharp transition from ferromagnetic to paramagnetic behaviour. However a drastic change in the temperature dependence of the susceptibility is observed for $x > 11.2$.

The Mössbauer spectra obtained at $T=4.2$ K are shown in fig. 3. The contribution of the unidentified second phase in the spectrum of LaFe$_{12}$Al is clearly observed and the outermost lines of this contribution are indicated by arrows in fig. 3. The unidentified phase
(≈ 40% of the sample) remains magnetically ordered at T=238 K as is shown in fig.4, while the other part of the sample is in the paramagnetic region. It is obvious that the spectrum of the sample with a nominal composition LaFe₄Al₉ really belongs to the compound LaFe₄Al₈ which crystallizes in the ThMn₁₂ type of structure [3]. The mean hyperfine fields deduced are listed in Table 1 and have been plotted in fig.1. The mean hyperfine field shows the same concentration dependence as the saturation magnetization from x = 11 to x = 8. However, for lower values of x, the mean hyperfine field levels off to the value observed for LaFe₄Al₈ (ThMn₁₂ structure), which compound orders antiferromagnetically [3]. The values of the magnetic ordering temperature (Tₘ) defined as the temperature at which the hyperfine splitting of the Mössbauer spectrum disappears are listed in Table 1 and also plotted in fig.1. A remarkable increase of Tₘ for x = 12 has been observed after a decrease from Tₘ = 250 K for x = 10 to Tₘ = 190 K for x = 11.

![Diagram](image)

4. Discussion

The heat of alloying between La and Fe is positive [4]. As a consequence a stable La-Fe intermetallic does not exist. A minimum amount of Al will be required to lead to a pseudo-binary compound of a negative heat of formation and in addition form a suitable structure to accommodate the size of each of the three constituent atomic species.

In the compounds LaFeₓAl₃₋ₓ the moment per Fe atom decreases with decreasing Fe concentration and behaves according to expectation for 8 ≤ x ≤ 11. However, for x ≤ 7 no net magnetization has been found at T=4.2 K while a magnetic hyperfine splitting is still observed in the Mössbauer spectrum. We believe that the loss of the net magnetization for x ≤ 7 is due to formation of a spin glass, which means that for decreasing Fe concentration the ferromagnetic exchange interaction is decreasing faster than the antiferromagnetic one. For x < 6 the ThMn₁₂ type of structure becomes favoured. The composition of the compound formed is LaFe₄Al₈, which orders antiferromagnetically [3]. It is interesting that at the low Fe concentration region not only the antiferromagnetic exchange interaction becomes relatively strong, as in LaFe₄Al₈, but also the magnetic hyperfine field approaches the value observed for LaFe₄Al₈ [3].

In the high Fe concentration region the susceptibility measurements indicate that the pseudo-binary compound is changing from entirely ferromagnetic ordering for x = 11.2 to an antiferromagnetic ordering for x ≥ 11.5. This picture is qualitatively consistent with the very low magnetic moment observed for x = 11.8 while still a large hyperfine field is observed at the Fe-site. The increase of the
magnetic moment for $x = 12$ is due to the large contamination of the sample with the so far unidentified second phase.

The opposite concentration dependencies of $T_c$ and magnetic moment (as observed for $10 \leq x \leq 11.2$) were claimed to be associated with the anomalous thermal expansion below $T_c$ found in Invar type alloys$^5$ and is also observed earlier by us in the compounds $\text{LaFe}_x \text{Si}_{13-x}$.$^2$ In these latter compounds we have observed a cusp like anomaly near $T_c$ in their temperature dependence of the resistivity. Similar measurements on the present samples are in progress. The weakening of the overall ferromagnetic coupling for the compounds in the range $10 \leq x \leq 11.2$ can be understood in terms of the site occupation of the Fe atoms in the $\text{NaZn}_13$ crystal structure in conjunction with the lattice constant decreasing with increasing iron content. Denoting the two Fe sites by $\text{Fe}(1)$ and $\text{Fe}(2)$ in the hypothetical compound $\text{LaFe}_{12}(1)\text{Fe}_1(2)$, an increasing Fe concentration in $\text{LaFe}_x \text{Al}_{13-x}$ will lead to a larger occupation of both sites and hence to a larger occupation of the $\text{Fe}(2)$ site. This site is characterized by a rather low Fe-Fe nearest neighbour separation and by a nearest neighbour configuration consisting of 12 Fe atoms. The $\text{Fe}(2)$ nearest neighbour configuration is in several respects not much different from that of Fe atoms in $\gamma$-Fe. In the latter antiferromagnetism prevails and this may explain why one can expect an increasing antiferromagnetic interaction by filling more of the $\text{Fe}(2)$ sites in $\text{LaFe}_x \text{Al}_{13-x}$.

The increase of the ordering temperature for $x > 11.2$ is not yet understood.

References