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Magnetic properties of Nd$_2$Co$_{17-x}$Al$_x$ compounds studied by magnetic measurements and neutron diffraction

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Abstract

The magnetic properties of Nd$_2$Co$_{17-x}$Al$_x$ compounds ($x = 2, 3$ and $4$) were studied by means of neutron diffraction and magnetic measurements. The refinement results of the neutron powder diffraction patterns show that there is a slight preference for the Al atoms to occupy the 18h site in the rhombohedral Th$_2$Zn$_{17}$ structure adopted by these compounds. By contrast, the 9d site is completely avoided by the Al atoms. From magnetic measurements it is derived that there is an almost linear decrease of the Curie temperature with Al concentration accompanied by a somewhat less strong decrease of the saturation moment at 4.2 K. For the compound with $x = 4$ we observed a spin reorientation transition slightly above room temperature.

Keywords: Nd$_2$Co$_{17-x}$Al$_x$ compounds; Magnetic properties; Neutron diffraction

1. Introduction

In several preceding investigations [1–3] we have used neutron powder diffraction to study the site occupation of non-magnetic elements M in rare earth compounds of the type R$_2$Fe$_{17-x}$M$_x$ (M = Al, Ga and Si). In all examples studied, quite substantial deviations from a statistical site distribution of the non-magnetic atoms over the four available Fe sites (6c, 9d, 18f and 18h) were observed. The preferred site occupation of the M elements, when studied as a function of concentration, has been most helpful for finding the origin of the initial Curie temperature enhancement observed in all these materials, since neither the presence of the so-called Fe-dumbbell pairs, nor the increase of the unit cell volume play an important role. In the present report we have extended our investigation to Co compounds of the same structure type.

2. Experimental

Samples of Nd$_2$Co$_{17-x}$Al$_x$ were prepared by arc melting from starting materials of at least 99.9% purity. After arc melting the samples were wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for 3 weeks at 900°C. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase and that their crystal structure corresponds to the rhombohedral Th$_2$Zn$_{17}$ structure type.

Neutron diffraction data were collected at room temperature on approximately 2 g samples using the position sensitive detector diffractometer at the University of Missouri Research Reactor. The neutron wavelength used in these experiments was 1.4783 Å obtained by means of a pressure bent perfect silicon (511) monochromator. Data were taken in a 2θ range extending from 5 to 105°.

The magnetic measurements were made on powdered material on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 6 T. The measurements above 300 K were made on a purpose-built magnetometer based on the Faraday principle, using polycrystalline lumps in order to avoid oxidation at elevated temperatures as far as possible.
3. Results

The powder neutron diffraction data were analyzed by the Rietveld method using the fullprof program for multiphase material [4]. The appropriate nuclear scattering lengths employed in the refinement (\(b_{\text{Nd}} = 0.769 \times 10^{-12}\) cm, \(b_{\text{Co}} = 0.249 \times 10^{-12}\) cm, \(b_{\text{Al}} = 0.3449 \times 10^{-12}\) cm) and the magnetic form factors used for Nd and Co were taken from the fullprof library. The \(\text{Nd}_{x}\text{Co}_{17-x}\text{Al}_x\) samples with nominal composition \(x = 2\) and \(3\) showed no detectable second phase, whereas the sample with nominal composition \(x = 4\) showed the presence of several percent of a second phase identified as \(\alpha\text--\text{Co(Al)}\). All remaining lines were indexed and refined on the basis of the rhombohedral Th\(_2\)Zn\(_17\) structure adopted by \(\text{Nd}_{x}\text{Co}_{17-x}\). The results of the Rietveld refinements are presented in Table 1.

Results of magnetic measurements showing the temperature dependence of the magnetisation are displayed in Fig. 1. It is seen that the magnetic ordering temperatures of the three compounds investigated decrease strongly with Al concentration. As the temperature dependences of the magnetisations were measured on polycrystalline lumps of material in relatively low magnetic fields the three curves shown have a somewhat uncommon shape, the most obvious features being slight increases of the magnetisation somewhat below the corresponding Curie temperatures. We attribute these uncommon features to the presence of a substantial magnetic anisotropy of the Co sublattice, since these effects were not observed when the measurements were repeated with free powder particles. The presence of a substantial anisotropy is supported by X-ray diffraction made by us on magnetically aligned powders, showing that there is a well-developed preferred moment orientation perpendicular to the c-direction in all three compounds at room temperature. The curve of the compound with \(x = 4\) shows a small cusp-like anomaly slightly above room temperature, indicative of a magnetic phase transition of the spin reorientation type.

The field dependence of the magnetisation at 4.2 K of the three compounds investigated is shown in Fig. 2. The Al substitution is seen to give rise to a fairly strong decrease of the magnetisation. This is seen more clearly in Fig. 3 where we have plotted the magnetic moment per formula unit \(\text{Nd}_{x}\text{Co}_{17-x}\text{Al}_x\) vs. Al concentration. For \(\text{Nd}_{x}\text{Co}_{17}\) we used the data compiled in Ref. [5].

### Table 1
Refinement results for \(\text{Nd}_{x}\text{Co}_{17-x}\text{Al}_x\),

<table>
<thead>
<tr>
<th>Parameter</th>
<th>(x = 2.05)</th>
<th>(x = 3.12)</th>
<th>(x = 4.02)</th>
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</thead>
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<tr>
<td>(a (\text{Å}))</td>
<td>8.4980(6)</td>
<td>8.5228(4)</td>
<td>8.5488(4)</td>
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<td>(c (\text{Å}))</td>
<td>12.3498(9)</td>
<td>12.3744(7)</td>
<td>12.4065(6)</td>
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<tr>
<td>(c/a)</td>
<td>1.4533</td>
<td>1.4519</td>
<td>1.4513</td>
</tr>
<tr>
<td>(V (\text{Å}^3))</td>
<td>772.374</td>
<td>778.427</td>
<td>785.212</td>
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<tr>
<td>(\text{Nd}, 6c, z)</td>
<td>0.3438(4)</td>
<td>0.3433(4)</td>
<td>0.3416(3)</td>
</tr>
<tr>
<td>(\text{Co}/\text{Al}, 6c, z)</td>
<td>0.1022(9)</td>
<td>0.0982(7)</td>
<td>0.0978(7)</td>
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<td>(\text{Co}/\text{Al}, 18f, x)</td>
<td>0.2862(6)</td>
<td>0.2883(6)</td>
<td>0.2886(5)</td>
</tr>
<tr>
<td>(\text{Co}/\text{Al}, 18h, x)</td>
<td>0.1696(6)</td>
<td>0.1692(5)</td>
<td>0.1698(4)</td>
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<tr>
<td>(\text{Co}/\text{Al}, 18h, z)</td>
<td>0.4884(7)</td>
<td>0.4878(6)</td>
<td>0.4877(5)</td>
</tr>
<tr>
<td>(\text{Al}, 6c (%))</td>
<td>16.2</td>
<td>21.0</td>
<td>27.5</td>
</tr>
<tr>
<td>(\text{Al}, 9d (%))</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>(\text{Al}, 18f (%))</td>
<td>13.2</td>
<td>18.0</td>
<td>25.8</td>
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<tr>
<td>(\text{Al}, 18h (%))</td>
<td>15.6</td>
<td>27.0</td>
<td>32.0</td>
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<tr>
<td>(R)-factor</td>
<td>4.56</td>
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<td>4.60</td>
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<tr>
<td>(R_w)-factor</td>
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<td>5.70</td>
<td>6.04</td>
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<tr>
<td>(R_m)-factor</td>
<td>8.72</td>
<td>10.90</td>
<td>8.97</td>
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<td>(x^2)</td>
<td>1.24</td>
<td>1.20</td>
<td>1.16</td>
</tr>
<tr>
<td>(\text{Nd}, 6c \text{WSCV}^*)</td>
<td>30.202</td>
<td>30.375</td>
<td>30.459</td>
</tr>
<tr>
<td>(\text{Co}, 6c \text{WSCV})</td>
<td>12.839</td>
<td>12.939</td>
<td>12.991</td>
</tr>
<tr>
<td>(\text{Co}, 9d \text{WSCV})</td>
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<td>11.021</td>
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<td>(\text{Co}, 18h \text{WSCV})</td>
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<td>11.933</td>
<td>12.134</td>
</tr>
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<td>(u), (\text{Nd}, 6c)</td>
<td>1.7(3)</td>
<td>1.9(3)</td>
<td>1.5(3)</td>
</tr>
<tr>
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<td>1.8(2)</td>
<td>1.8(2)</td>
<td>1.0(2)</td>
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<td>(u), (\text{Co}, 9d)</td>
<td>1.5(1)</td>
<td>1.5(1)</td>
<td>1.4(1)</td>
</tr>
<tr>
<td>(u), (\text{Co}, 18f)</td>
<td>1.0(1)</td>
<td>1.0(1)</td>
<td>1.1(2)</td>
</tr>
<tr>
<td>(u), (\text{Co}, 18h)</td>
<td>1.5(1)</td>
<td>1.4(2)</td>
<td>1.4(2)</td>
</tr>
<tr>
<td>(\alpha\text--\text{Co(Al) (vol. %)})</td>
<td>0.00</td>
<td>0.00</td>
<td>8.39</td>
</tr>
</tbody>
</table>

* WSCV, Wigner–Seitz cell volume.

Fig. 1. Temperature dependence of the magnetisation of the compounds \(\text{Nd}_{x}\text{Co}_{17-x}\text{Al}_x\) measured in a field of 0.1 T.

4. Discussion

The concentration dependence of the Curie temperature is shown in Fig. 4. The Curie temperature is seen to decrease almost linearly with Al concentration. This behaviour is in strong contrast with that observed in \(\text{Nd}_{x}\text{Fe}_{17-x}\text{Al}_x\), where the Curie temperature first increases strongly with \(x\) before decreasing at higher \(x\).
values ($x > 4$). The reason for this difference in behaviour is probably associated with the fact that no antiferromagnetic intermetallic compounds based on Co are known. This, in turn, could mean that the magnetic coupling between Co moments in metal systems is always ferromagnetic, independent of Co moment and structure, leaving no room for antiferromagnetic types of 3d moment interaction that could reduce the Curie temperature. The latter feature is frequently invoked to explain the abnormally low Curie temperature in R$_2$Fe$_{17}$ compounds and their enhancement by Al substitution.

One of the characteristic features of the crystal structure of the Nd$_2$Co$_{17}$ compounds is the presence of so-called dumbbell pairs of Co atoms. These Co atoms occupy the crystallographic 6c position. We have already mentioned that one does not expect any particular influence of their presence on the Curie temperature. Apparently, these Co atoms do, however, have an important effect on the magneto-crystalline anisotropy of this class of materials. Earlier investigations by Yajima and Hamano [6] and Desportes et al. [7] showed that the presence of these dumbbell atoms is most likely responsible for the easy-plane anisotropy of the Co sublattice in the R$_2$Co$_{17}$ compounds, compared to the easy-axis anisotropy in the RCo$_5$ compounds. It can be seen from the results shown in Table 1 that a substantial fraction of the Co atoms at the 6c sites is replaced by Al atoms. This opens the possibility that the Co sublattice anisotropy becomes the easy-axis type for sufficiently high Al concentrations. When going from the Curie temperatures to lower temperatures, the crystal-field-induced rare earth sublattice anisotropy grows in importance. At all but the lowest temperatures, this latter anisotropy will be determined by the second order crystal field parameter $A_2^2$ which is negative [5]. This means that when lowering the temperature, the easy-axis Co sublattice anisotropy has to compete with the Nd sublattice anisotropy favouring a preferred moment direction perpendicular to the c-axis. The occurrence of a spin reorientation will be the result when the latter becomes predominant. This may explain the spin reorientation observed in the compound with the highest Al concentration studied by us. Our interpretation is in agreement with the observation that the preferred moment direction changes from planar to axial with increasing $x$ in Y$_2$Co$_{17-x}$Al$_x$ [8].

References


