

## Magnetic Properties of $\text{Ln}_3\text{In}$ Intermetallic Compounds\*

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Received January 25, 1973

Results of magnetic studies of  $\text{Ln}_3\text{In}$  phases ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Gd}, \text{Dy}$  and  $\text{Er}$ ) are presented. All materials exhibited Curie-Weiss behavior in the paramagnetic regions with effective moments approximating  $g[J(J+1)]^{1/2}$  for the tripositive ion. Positive Weiss constants were observed indicating predominance of ferromagnetic exchange.  $\text{Pr}_3\text{In}$  and  $\text{Nd}_3\text{In}$  order ferromagnetically at 62 and 114 K, respectively. However, the ordered moment is less than 10% of  $gJ$ .  $\text{Dy}_3\text{In}$  and  $\text{Er}_3\text{In}$  also seem to order ferromagnetically, but with low moments compared to  $gJ$ .  $\text{Gd}_3\text{In}$  exhibits metamagnetic behavior with a critical field of about 5 kOe. Neutron diffraction measurements on  $\text{Nd}_3\text{In}$  indicate that it is ferromagnetic and confirm the low  $\text{Nd}^{3+}$  moment.

Magnetic studies of the rare-earth intermetallics involving indium have been limited in the past to the series  $\text{LnIn}_3$  ( $I$ ). These compounds form in the  $\text{Cu}_3\text{Au}$  structure and they exhibited tendency for antiferromagnetic order. It seemed of interest to examine the  $\text{Ln}_3\text{In}$  compounds for comparison with the  $\text{LnIn}_3$  series. Although the crystal structure was not known for the whole series, at least one compound,  $\text{Pr}_3\text{In}$ , was known to crystallize in the  $\text{Cu}_3\text{Au}$  structure (2).

### Experimental Details

The compounds were prepared by induction heating in  $\text{MgO}$  crucibles. X-ray diffraction patterns indicated that the samples were single phase, at least in the case of the light rare-earth compounds investigated ( $\text{Pr}, \text{Nd}$ ). These compounds were indexed as fcc structures. The lattice parameters are 4.90 and 4.93 Å for  $\text{Pr}_3\text{In}$  and  $\text{Nd}_3\text{In}$ , respectively. There is a structural

change in the series at  $\text{Gd}_3\text{In}$ . The phases containing heavy rare-earths ( $\text{Gd}, \text{Dy}, \text{Er}$ ) could not be indexed as cubic structures. However, the patterns were simple when compared to those expected for orthorhombic or hexagonal structures, in which rare-earth intermetallics are frequently found to form. Neutron diffraction patterns on  $\text{Nd}_3\text{In}$  were obtained at room temperature and at 4.5 K.

### Results and Discussion

The bulk magnetic results are summarized in Table I. Curie-Weiss behavior was observed in the paramagnetic region with effective moments in good agreement with that expected for free tripositive ions. The Weiss constants ( $\theta_p$ ) are positive, indicating the predominance of ferromagnetic exchange. Results for  $\text{Pr}_3\text{In}$  and  $\text{Nd}_3\text{In}$  indicate ferromagnetic ordering with Curie temperatures at 62 and 114 K, respectively, as shown by the magnetization versus temperature results in Fig. 1.

Figure 2 shows the thermomagnetic results for  $\text{Gd}_3\text{In}$ . The three curves demonstrate the peculiar

\* The work at the University of Pittsburgh was assisted by a contract with the U.S. Atomic Energy Commission.

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TABLE I  
MAGNETIC RESULTS FOR  $\text{Ln}_3\text{In}^a$

Compound	$T_c$ (K)	$\mu_{\text{eff}}$	$g[J(J+1)]^{1/2}$	$\mu_{\text{or}}$ ( $H = 20$ kOe)	$\theta_p$ (K)
$\text{Pr}_3\text{In}$	62	3.5	3.58	0.23	9.3
$\text{Nd}_3\text{In}$	114	3.4	3.62	0.37	10
$\text{Gd}_3\text{In}$	213	8.8	7.94	5.2	196
$\text{Dy}_3\text{In}$	138	10.4	10.6	5.8	113
$\text{Er}_3\text{In}$	51	9.6	9.6	5.1	31

<sup>a</sup> Moments ( $\mu_{\text{eff}}$  and  $\mu_{\text{or}}$ ) are given as  $\mu_B/\text{rare-earth atom}$ .

magnetic behavior of this compound. At 18 kOe the magnetization-temperature behavior of this compound is characteristic of a ferromagnetically ordered material with a fairly high Curie point, approximately 200 K. At lower fields of 5.3 kOe and 1.1 kOe, maxima are seen in the magnetization versus temperature curves at 81 and 112 K. Magnetization versus field strength data are

given in Fig. 4. The behavior of  $\text{Gd}_3\text{In}$  is indicative of metamagnetism for this material. Figure 3 shows the thermomagnetic data of  $\text{Dy}_3\text{In}$  and  $\text{Er}_3\text{In}$  with Curie points indicated at about 140 and 50 K, respectively. The magnetization versus field results in Fig. 4 give no indication of metamagnetic behavior for these materials.

Ordering temperatures are in the range

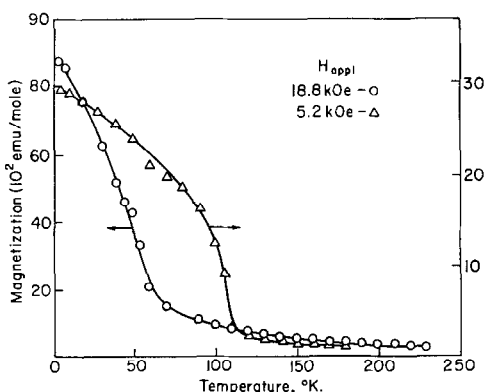


FIG. 1. Magnetization versus temperature for  $\text{Pr}_3\text{In}$  (o) and for  $\text{Nd}_3\text{In}$  ( $\Delta$ ).

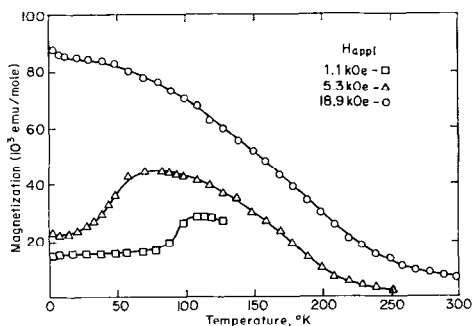


FIG. 2. Magnetization versus temperature for  $\text{Gd}_3\text{In}$ .

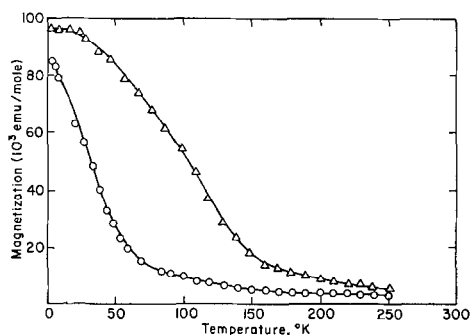


FIG. 3. Magnetization versus temperature for  $\text{Dy}_3\text{In}$  ( $\Delta$ ) and  $\text{Er}_3\text{In}$  (o) at 18.8 kOe applied field.

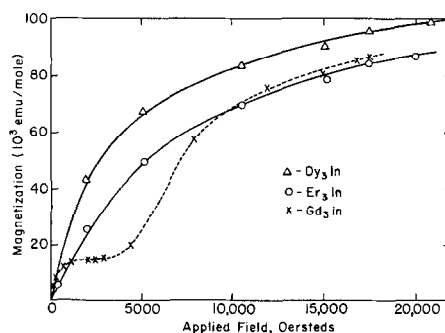


FIG. 4. Magnetization versus applied field for  $\text{Gd}_3\text{In}$  ( $\times$ ),  $\text{Dy}_3\text{In}$  ( $\Delta$ ) and  $\text{Er}_3\text{In}$  (o) at 4.2 K.

expected when only lanthanide-lanthanide interactions are involved. In this respect the compounds can be regarded as normal. However, the measured saturation moments of  $\text{Pr}_3\text{In}$  and  $\text{Nd}_3\text{In}$  are quite abnormal in the sense that they are a small fraction,  $\sim 10\%$ , of the expected  $gJ$  value. There are at least three views of the low measured moments: (a) they may be real; (b) the measured value may be incorrect due to lack of saturation; (c) the low moments may be a consequence of a noncollinear magnetic structure. To decide among these possibilities neutron diffraction measurements were made on  $\text{Nd}_3\text{In}$ .

The neutron diffraction data at 300 and 4.5 K show a small increase in all of the reflection intensities at the lower temperature. This increase is larger than can be attributed to the Debye or thermal factor and represents a small ordered ferromagnetic moment in the magnetic structure of  $\text{Nd}_3\text{In}$ . An approximate analysis of the reflection intensities indicates an ordered moment  $\leq 0.5 \mu_B$  at the Nd atom sites. No superlattice or extraneous reflections were observed at 4.5 K which indicates that the compound is not antiferromagnetic or ferrimagnetic. Therefore, the moments reported in Table I must be regarded as real.

The low  $\text{Nd}^{3+}$  moment is of considerable interest. It is undoubtedly a consequence of the influence of the crystal field on the  $\text{Nd}^{3+}$  ion. The neodymium ion in  $\text{Nd}_3\text{In}$  occupies a site of tetragonal symmetry. Detailed calculations such as have been made for ions in cubic (3) or hexagonal (4) symmetry have not been made for  $\text{Nd}^{3+}$  in a site of tetragonal symmetry. Consequently a quantitative accounting for the low moment cannot be made as yet. We note, how-

ever, that one of the Kramers doublets comprising one of the  $\Gamma_8$  quartets has a moment of  $0.40 \mu_B$ , which is close to the measured neodymium moment. If this state  $[b_1|-5/2\rangle + b_2|3/2\rangle$  according to Lea, Leask and Wolf (3) splits off as the ground state in  $\text{Nd}_3\text{In}$ , one would have a basis for accounting for the low observed moment.

It should be emphasized that a proper analysis of the magnetism of  $\text{Nd}_3\text{In}$  entails calculations similar to those of Schumacher and Hollingsworth (5) for cubic symmetry or of Segal and Wallace (6) for hexagonal symmetry. In these treatments the Hamiltonian includes the influence of both the crystalline electric field and the magnetic field. Since the Curie temperature is high, the internal field in  $\text{Nd}_3\text{In}$  must be quite large. The low  $\text{Nd}^{3+}$  moment implies that the crystal field must be quite strong in  $\text{Nd}_3\text{In}$  [comparable to, or perhaps larger, for example, than the 200 to 400 K overall splitting observed for  $\text{PrIn}_3$  (1)] for were it not we should observe nearly the full ion moment,  $3.27 \mu_B$ .

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