

## FERROMAGNETISM IN SOLID SOLUTIONS OF SCANDIUM AND INDIUM

B. T. Matthias, A. M. Clogston, H. J. Williams, E. Corenzwit, and R. C. Sherwood  
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received June 12, 1961)

We have found that a solid solution of approximately 24 atomic percent indium in scandium becomes ferromagnetic below 6°K. The ferromagnetism occurs over an extremely narrow range of compositions between  $\text{Sc}_{0.762}\text{In}_{0.238}$  and  $\text{Sc}_{0.758}\text{In}_{0.242}$ , a change of 0.4 atomic percent of indium.

The ferromagnetism of these solid solutions was encountered during a search for superconductivity in the scandium-indium system. After the discovery that  $\text{La}_3\text{In}$  becomes superconducting at 10.4°K,<sup>1</sup> the corresponding phases of yttrium and scandium became of interest. While In is not soluble in Y, no difficulty has been found in dissolving In in Sc simply by melting the materials together in an arc furnace. Measurements of the susceptibility of these melts initially showed a maximum near 20 atomic percent In. After the ingots were annealed for a week at 800°C the maximum susceptibility increased greatly and moved to higher In concentrations. No superconductivity has been found in this system. X-ray patterns do not show the cubic  $\text{La}_3\text{In}$  phase but instead the essentially hexagonal close-packed symmetry of scandium metal, with a smaller lattice constant, consistent with a smaller atomic radius for metallic indium than for scandium. At the composition  $\text{Sc}_{0.70}\text{In}_{0.30}$  the structure changes.

In Fig. 1 we show a plot of the magnetic moment in cgs units per gram observed in a field of 14 000 gauss at 1.4°K as a function of the atomic fraction of In for the annealed samples. The extreme sharpness of the peak shows how very easy it would be to miss the occurrence of ferromagnetism in this system. Measurements have been made of the susceptibilities  $\chi$  for these solid solutions from 1.4°K to room temperature.  $\chi$  is strongly temperature dependent, becoming large at low temperatures, and can be fitted approximately to a Curie-Weiss law of the form  $\chi = N\mu_B^2 p_{\text{eff}}^2 / 3k(T-\theta)$  where  $N$  is the number of magnetic centers,  $\mu_B$  is the Bohr magneton,  $p_{\text{eff}}$  is the effective magnetic moment per atom, and  $\theta$  is the Curie temperature. The values of  $p_{\text{eff}}$  and  $\theta$  are shown as a function of composition in Figs. 2 and 3 and in Table I. Although  $p_{\text{eff}}$  shows a small peak at the critical composition, the large peak in the mag-

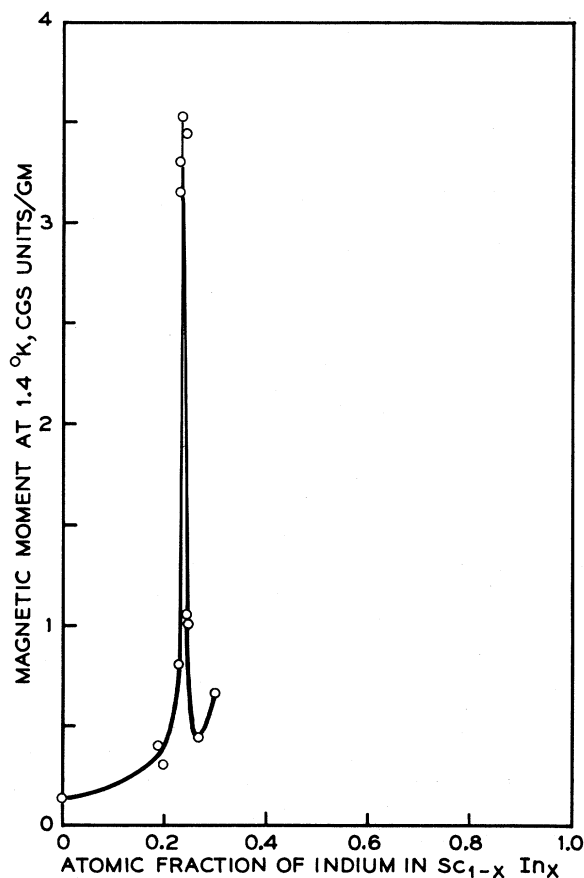


FIG. 1. Magnetic moment per gram observed at 1.4°K in a field of 1400 gauss with a sample of  $\text{Sc}_{1-x}\text{In}_x$  as a function of atomic fraction of In.

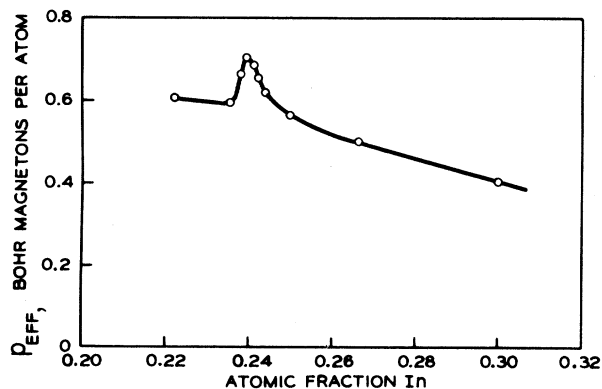


FIG. 2. Effective magnetic moment in Bohr magnetons per atom for  $\text{Sc}_{1-x}\text{In}_x$  as a function of atomic fraction of In, determined by fitting observed susceptibilities to a Curie-Weiss law.

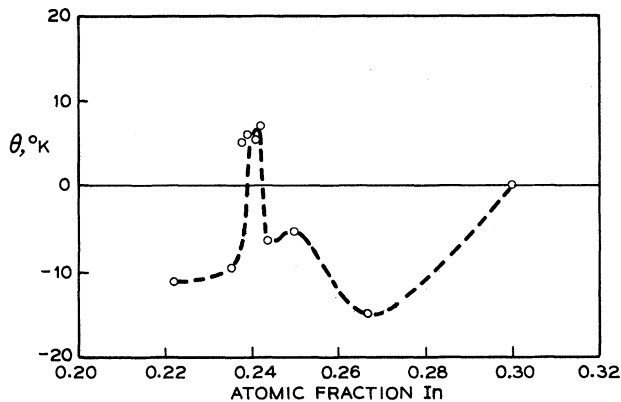


FIG. 3. Curie-Weiss constant  $\theta$  in degrees Kelvin of a sample of  $\text{Sc}_{1-x}\text{In}_x$ , as a function of atomic fraction of In, determined by fitting observed susceptibilities to a Curie-Weiss law.

netic moment shown in Fig. 1 clearly arises from the fact that  $\theta$  becomes positive at this point. The accuracy in determining  $\theta$  is not better than 1 or 2°K.

A positive value of  $\theta$  implies that the material must become ferromagnetic for  $T < \theta$ . For the four samples where  $\theta$  is positive, the magnetic moment has been studied as a function of  $H$  and  $T$ . The Curie temperature  $T_C$  has been determined by plotting  $H/\sigma_g$  vs  $\sigma_g^2$  isotherms, where  $\sigma_g$  is the magnetization per gram. These results are given in Table II along with the saturation moment  $\mu_a$  per atom in Bohr magnetons. We also show the magnetic moment per atom determined from the Curie-Weiss law assuming  $g=2$ . Remanence has been observed at 1.4°K.

The nature of the ferromagnetic state in  $\text{Sc}_{0.76}\text{In}_{0.24}$  is not clear at this point. The Curie-Weiss law obeyed by the susceptibilities suggests that the scandium  $d$  electrons are partially localized and exhibit a small magnetic moment.

Table I.  $\theta$  and  $p_{\text{eff}}$  for  $\text{Sc}_{1-x}\text{In}_x$  as a function of  $x$ .

$x$	$p_{\text{eff}}$	$\theta^\circ\text{K}$
0.222	0.60	-11
0.235	0.60	-10
0.238	0.66	+5
0.240	0.70	+6
0.241	0.69	+6
0.242	0.65	+7
0.244	0.62	-6
0.250	0.56	-5
0.267	0.50	-15

If this were the case we would have a ready explanation of the fact that no superconductivity develops in this system in contrast to the high superconducting transition temperature of  $\text{La}_2\text{In}$ . This model, however, provides no explanation why ferromagnetism should appear in such an extremely narrow range of compositions.

The sensitivity to composition and homogeneity is perhaps suggestive of a band-filling mechanism, leading to itinerant electron ferromagnetism. A similar situation has been reported previously for  $\text{ZrZn}_2$ ,<sup>2</sup> which becomes ferromagnetic below 35°K.

In this case, Abrahams<sup>3</sup> could not detect the 1.4 Bohr magnetons per atom indicated by the Curie-Weiss law although his measurements were consistent with the smaller value of  $0.17 \mu_B$  determined by measurements of the saturation magnetization. Electrical resistivity measurements by Olsen<sup>4</sup> also failed to show any spin disorder scattering above the Curie temperature. The ferromagnetism of  $\text{ZrZn}_2$  is easily destroyed by impurities and other lattice disturbances.

An attempt to account for the ferromagnetism of the Sc-In system by an itinerant electron model, however, also faces difficulties. It is easy to show that the susceptibility of the band model above the Curie temperature will be given, in the Hartree-Fock approximation, by the expression

$$\frac{1}{\chi} = \frac{1}{\chi_0(T)} - \frac{\Omega}{2\mu_B^2} J, \quad (1)$$

where  $\chi_0(T)$  is the temperature-dependent susceptibility that would prevail in the absence of exchange,  $\Omega$  is the atomic volume, and  $J$  is approximately the exchange self-energy of an electron on one lattice site. If the band in question is fairly wide,  $\chi_0(T)$  and  $\chi$  will be essentially temperature independent, contrary to our observations. If the band is narrow enough to introduce substantial temperature variations in  $\chi_0(T)$ , it will still be difficult to match the shape of the observed susceptibility curves using Eq. (1) since experimental-

Table II.  $T_C$  and  $\mu_a$  for  $\text{Sc}_{(1-x)}\text{In}_x$  as a function of  $x$ .

$x$	$T_C^\circ\text{K}$	$\mu_a$ (Bohr magnetons)	$(1+p_{\text{eff}}^2)^{1/2}-1$
0.238	5	0.035	0.20
0.240	6	0.036	0.22
0.241	6	0.039	0.22
0.242	6	0.038	0.18

ly  $\chi$  is rising sharply at the lowest temperatures.

The narrow range of compositions for which ferromagnetism exists in the Sc-In system suggests that this kind of ferromagnetism may be a more general phenomenon than has been thought until now, and may be found to occur in other systems.

We would like to thank Mrs. V. B. Compton

for her x-ray investigations of these alloys.

<sup>1</sup>B. T. Matthias, V. B. Compton, and E. Corenzwit, *J. Phys. Chem. Solids* **19**, 130 (1961).

<sup>2</sup>B. T. Matthias and R. M. Bozorth, *Phys. Rev.* **109**, 604 (1958).

<sup>3</sup>S. C. Abrahams, *Z. Krist.* **112**, 427 (1959).

<sup>4</sup>C. E. Olsen, *J. Phys. Chem. Solids* **19**, 660 (1961), and to be published.

## SHIFT OF NUCLEAR QUADRUPOLE RESONANCE FREQUENCY BY ELECTRIC FIELD

Toshimoto Kushida\* and Kuniomi Saiki†

Hiroshima University, Hiroshima, Japan

(Received June 14, 1961)

It is well known that a static magnetic field splits the nuclear quadrupole resonance (NQR) lines in a single crystal.<sup>1</sup> One might immediately think of the similar effect caused by an electric field applied to the specimen. As a matter of fact, Pound<sup>2</sup> applied a field of about 50 000 v/cm across a thin plated-shaped single crystal of potassium iodide, but no shift in the resonance frequency nor change in the line shape was observed in the  $I^{127}$  nuclear resonance line. Gutowsky and Williams<sup>3</sup> tried to observe the effect of an electric field on an NQR line of the Cl nucleus in  $\text{NaClO}_3$  single crystal without success.

Recently Bloembergen<sup>4</sup> pointed out the possibility of observing the change in the quadrupole coupling constant caused by an external electric field, if the crystal lattice has no local inversion symmetry about the pertinent nucleus.

It is the purpose of this Letter to report the successful observation of this effect for the  $\text{Br}^{81}$  NQR line in a single crystal of  $\text{NaBrO}_3$ .<sup>5</sup> The resonance frequency and the line shape are observed as a function of applied electric field using a regenerative spectrometer<sup>6</sup> in conjunction with a precise 0°C ice bath in order to keep the temperature of the sample constant during the run. Aluminum film electrodes are evaporated on the surfaces of a thin plate sample which has been cut from a larger single crystal.

The peak frequency of the line shifts linearly with the applied field  $E$  when  $E$  is parallel to  $[111]$ , whereas no shift in the center frequency is observed in the case of  $E \parallel [100]$ . Reversal of the polarity of  $E$  reverses the sign of the shift. A typical example of the observed absorption curve is shown in Fig. 1. Here  $E$  is along the

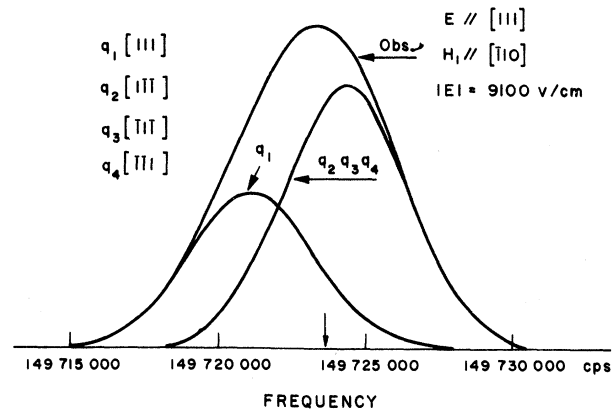


FIG. 1. The effect of the electric field on the  $\text{Br}^{81}$  resonance in  $\text{NaBrO}_3$  single crystal. The arrow  $\downarrow$  indicates the center frequency of the original line without the field.

$[111]$  direction of the crystal, and  $H_1$ , an rf magnetic field in a sample coil of the spectrometer, is applied along the  $[\bar{1}10]$  direction. The vertical arrow  $\downarrow$  indicates the center frequency without the electric field. The line shape, which was symmetric without an  $E$  field, is slightly asymmetric, and the center frequency has shifted by about 500 cps.

A cubic unit cell<sup>7</sup> of  $\text{NaBrO}_3$  has four physically inequivalent, but chemically equivalent,  $\text{BrO}_3^-$  radicals. The maximum principal axes of electric field gradients about Br nuclei are parallel to the body diagonals of the unit cell. The field gradients along the  $[111]$ ,  $[\bar{1}\bar{1}\bar{1}]$ ,  $[\bar{1}1\bar{1}]$ , and  $[\bar{1}\bar{1}1]$  directions will be denoted, respectively, by  $q_1$ ,  $q_2$ ,  $q_3$ , and  $q_4$ .

The distortions of the field gradients produced