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Crystallographic and Magnetic Characteristics of the $Y_2Ni_{17-x}Cu_x$ System†

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Crystallographic and magnetic characteristics of ternaries represented by the formula $Y_2Ni_{17-x}Cu_x$ have been determined in an effort to establish why ferromagnetism in Y_2Ni_{17} (and also in Lu_2Ni_{17}) is lost with increasing temperature in two stages. The *a* and *c* spacings both increase with increasing x (i.e., replacement of Ni by Cu). The saturation magnetization and the two transition temperatures decrease with increasing x. The initial decrease in saturation magnetization suggests that Cu transfers all its *s* electrons to Ni, whereas for $x > 2.6$ the decrease indicates a transfer of only 0.4 electron per Cu atom.

Magnetization versus field at 4°K shows two stages for certain of the ternaries. These results and the temperature dependence of magnetization are interpreted to indicate that there is an equilibrium between *s* and *d* electrons that is temperature and field sensitive for values of x between 2.5 and 3. Interpretations developed for the ternaries have been extended to Y_2Ni_{17}. The two stages of magnetization are ascribed to a change of electronic configuration of Ni (lower transition) with concurrent change in moment and normal destruction of magnetic order at the upper transition point. The lower transition resembles the situation in elemental Ce where a change from the +4 to the +3 state is brought on by changing temperature.

I. Introduction

Considerable attention has been paid (*1*) in recent years to intermetallic compounds represented by the formula Ln_2T_{17}, in which Ln represents one of the lanthanide elements and T is Fe, Co or Ni. Interest in these intermetallics is partly due to the fact that they are a new class of compounds and partly to their close structural relationship to the $LnCo_{5-x}Cu_x$ ternaries now being found useful as permanent magnetic materials (*2*, *3*). The present work is an outgrowth of an earlier study of Ln_2Ni_{17} compounds (*4*) in which it was revealed that with rising temperature ferromagnetism is lost in two stages in the supposedly straightforward Y_2Ni_{17} and Lu_2Ni_{17} compounds (Fig. 1). The first demagnetization step occurs at T ~ 175°K and the second at T ~ 600°K. Two suggestions for this unusual magnetization–temperature behavior were advanced (*4*).

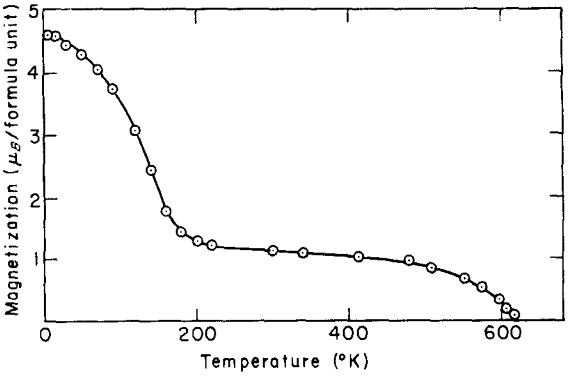

FIG. 1. Magnetization versus temperature for Y_2Ni_{17} for an applied field of 18.5 kOe.

First, the Y_2Ni_{17} and Lu_2Ni_{17} compounds are assumed to have the Th_2Ni_{17} (*5*) type hexagonal structure. However, the Ni atomic positions were not experimentally determined (*5*) for the Th_2Ni_{17} compound; rather it was assumed that they occupied ideal positions derived from the structurally related 1:5 hexagonal structure. The space group assignment ($P6_3/mmc$) is the highest symmetry, centrosymmetric space group allowed by the systematic extinction observed, (*hh.l*) for odd *l* only. If a lower symmetry space group represents the true symmetry of the Y_2Ni_{17} structure, the Ni–Ni planar bond distances are not required by symmetry to be equivalent. The two demagnetization steps could

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then be due to unequal Ni–Ni magnetic interactions, caused by nonequivalent Ni–Ni planar bond distances. There is some question about the assignment of the Th_2Ni_{17} structure type from x-ray powder diffraction patterns (*6*). To date, no single crystal structure determination of a representative 2:17 compound with the Th_2Ni_{17} type structure has been made; Y_2Ni_{17} (and Lu_2Ni_{17}) have been assigned to this structure type only because a satisfactory fit of the powder diffraction patterns is obtained on this basis. Single crystal structure determination is necessary to establish definitely the structure.

Second, it was suggested that the initial demagnetization step might result from a change in magnetic structure. From the saturation moment value at 4.2°K, it seemed clear that the moments are aligned parallel. At the initial demagnetization temperature (~ 175°K) the moment could rearrange to a canted orientation, with a final break-up of magnetic order at the second demagnetization temperature, ~ 600°K.

It was thought that some insight into this double demagnetization of Y_2Ni_{17} might be provided if the strong Ni–Ni interaction could be weakened. Weakening of this interaction was brought about by the replacement of Ni by Cu to form the ternary system $Y_2Ni_{17-x}Cu_x$, whose magnetic and crystallographic characteristics are reported in this communication.

II. Experimental Techniques

The $Y_2Ni_{17-x}Cu_x$ compounds were prepared by levitation melting of stoichiometric proportions of the highest purity metals obtainable commercially (99.9% or better). All samples were annealed under vacuum in sealed Vycor ampoules at appropriate temperatures (800–950°C). X-ray powder diffraction patterns were obtained using a GE-XRD 5 diffractometer to confirm structure and determine cell dimensions.

Magnetic measurements were made by the Faraday method. Two separate units were used to obtain the magnetization–temperature data. The apparatus used for the below room temperature measurements (4.2 to ~ 300°K) has been described elsewhere (*7*). A similar unit was built (*8*) to enable measurements to be made in the temperature range from room temperature up to 1000°C.

Saturation moments were obtained using an extrapolation of the measured magnetization versus the reciprocal of the effective field (H_{eff}) to $1/H_{\text{eff}} = 0$. Curie temperatures were obtained by the extrapolation of the linear portion of the magnetization (σ) squared versus the temperature to $\sigma^2 = 0$.

III. Experimental Results

Room temperature powder x-ray diffraction patterns confirmed that all compounds formed (up to $x = 5.70$) were single phase; moreover these data were consistent with the Th_2Ni_{17} type hexagonal structure. No diffraction peaks due to free Ni or Cu were observed. The composition range above $x = 5.70$ was not investigated. Lattice parameters calculated from the diffraction patterns are shown in Fig. 2. Expansion of both the *a*- and *c*- lattice parameters was observed with the addition of Cu.

The addition of Cu in the $Y_2Ni_{17-x}Cu_x$ system produced an initial linear decrease in the saturation moment (μ_{sat}) at 4.2°K and a monotonic decline in the upper demagnetization or transition temperature (Fig. 3). The linear decrease of μ_{sat} is ascribed to the filling of the holes in the Ni 3d band. Similar results were found in the Cu–Ni alloy system (*9*) for concentrations of Cu less than 58 at. %, the saturation magnetization being lowered by 1.0 μ_B for each Ni replaced. The decrease of the Curie temperature in Cu–Ni alloys is associated with the weakening of exchange due to the substitution of Cu for Ni. Again similar results are observed for the $Y_2Ni_{17-x}Cu_x$ ternary system and the Ni–Cu alloy system.

The Cu concentration required to render the nickel nonmagnetic can be estimated based on two assumptions: (1) that Cu donates one electron to Ni thus leaving Ni in the $3d^{10}4s^{0.6}$ configuration and Cu devoid of *s* electrons, or (2) that Cu donates 0.4 electron to Ni and, hence, both Cu and Ni are left

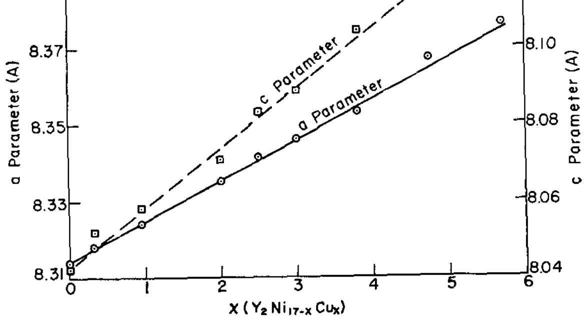

FIG. 2. Lattice parameters versus composition for the $Y_2Ni_{17-x}Cu_x$ system. The left ordinate axis is for the *a* parameter.

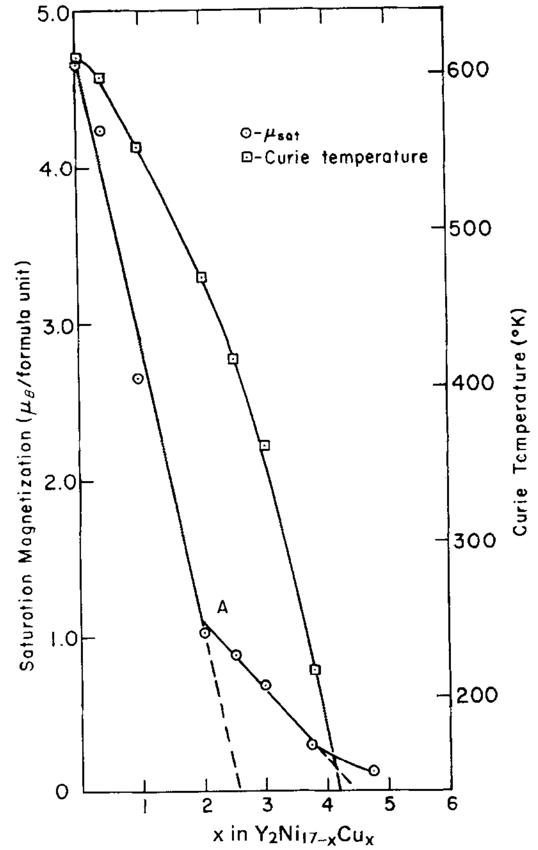

FIG. 3. Saturation moment (measured at 4.2°K) and upper transition temperature (Curie temperature) versus composition. For x between 0 and 2 Cu seems to transfer all its s electrons to Ni whereas for x between 2 and 4 it transfers only 0.4 electron per atom (see text).

in a $3d^{10}4s^{0.6}$ configuration. (Assumption 2 is consistent with the simple concept of the loss of ferromagnetism in elemental nickel by alloying with Cu.) The initial linear portion of the μ_{sat} versus composition curve for the $Y_2Ni_{17-x}Cu_x$ system approximates the calculated concentration of Cu necessary to render the Ni atoms nonmagnetic according to Assumption 1 above. At $x \approx 2$ there is a break in the curve and a second linear region is observed extrapolating to $x = 4.5$, which is very close to the composition required for nonmagnetic nickel according to Assumption 2 above, namely $Y_2Ni_{12.8}Cu_{4.2}$. For larger Cu concentrations it is found that a moment still exists. The presence of this moment closely follows the results found in the Cu–Ni alloy system (and other Ni alloy systems). Goldman and Arrott (*10*) have shown that Cu–Ni alloys are ferromagnetic for Cu concentrations up to 63% and paramagnetic at low temperatures between 63 and 97.5% Cu. The existence of paramagnetism at these higher Cu concentrations has been attributed to sample inhomogeneity on a microscopic scale. Due to statistical fluctuations in disordered substitutional solid solutions, regions of relatively high- and low-Ni concentration exist within the sample. The bulk magnetic properties at high Cu concentrations result from those portions of the sample in which the Ni concentration is above the value of the hypothetical homogeneous alloy. Noting the basic similarities of the Cu–Ni alloy system and the $Y_2Ni_{17-x}Cu_x$ ternary compounds[1] it is likely that similar considerations hold.

The magnetization versus field strength (field dependency) at 4.2°K for the $Y_2Ni_{17-x}Cu_x$ ternaries showed normal ferromagnetic saturation for $x = 0.38$, 0.95, 3.00 and 3.80; however, for $x = 2.00$ and 2.50 the field dependency at 4.2°K showed a second

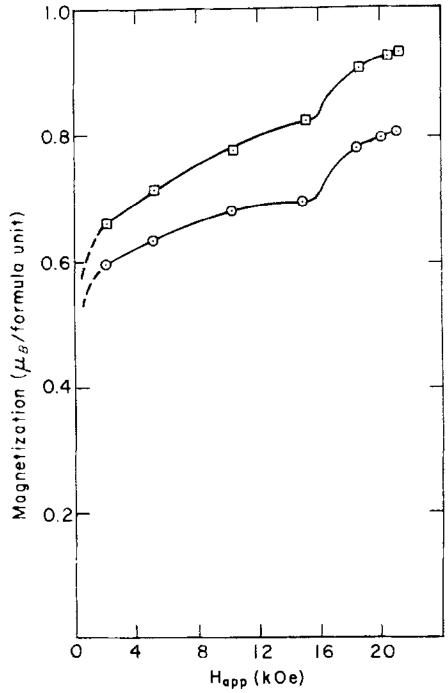

FIG. 4. Magnetization versus applied field strength for $Y_2Ni_{15}Cu_2$ □ and $Y_2Ni_{14.5}Cu_{2.5}$ ○ at 4.2°K.

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[1] It is of interest to note that A. W. ABEL and R. S. CRAIG *in J. Less-Common Metals* **16**, 77 (1968) have reported the magnetic behaviour of $YFe_{2-x}Co_x$ to be very similar to that of Fe–Co alloys. Their results and those obtained in the present study suggest that properties of binary systems of metals of the First Long Period carry over into ternary systems when the third component is yttrium.

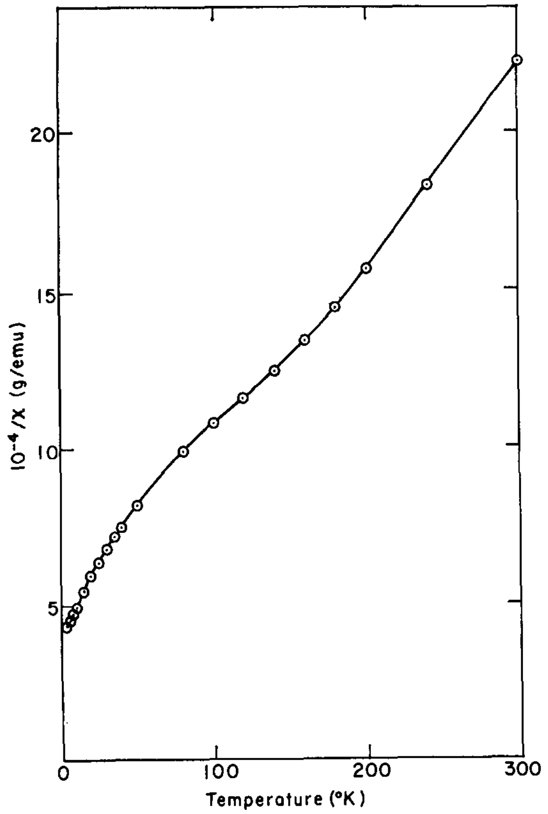

FIG. 5. Inverse susceptibility versus temperature for $Y_2Ni_{12.25}Cu_{4.75}$ measured at 18.5 kOe.

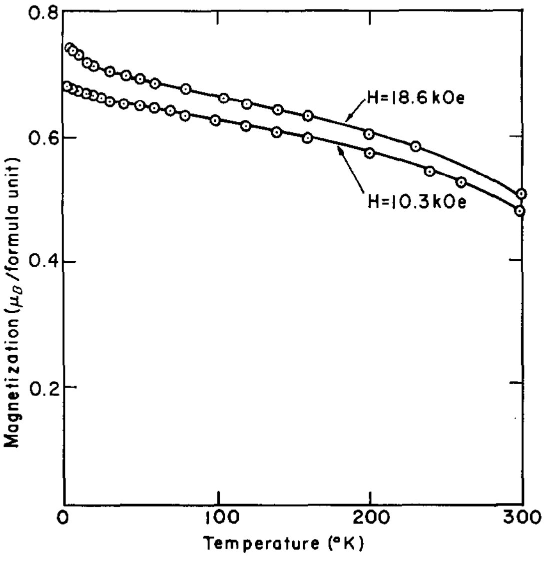

FIG. 6. Magnetization–temperature behavior of $Y_2Ni_{14.5}Cu_{2.5}$ at field strengths above and below the critical field (~ 16 kOe).

significant rise in the magnetization at higher field strength (Fig. 4). At still higher Cu concentrations, $x = 4.75$ and $x = 5.70$ there was no evidence of magnetic ordering, but there were deviations from Curie–Weiss behavior (Fig. 5).

The magnetization–temperature behavior of the $Y_2Ni_{14.5}Cu_{2.5}$ sample was established at $H > H_c$ and $H < H_c$, where H_c is the field strength at which the second rise in the field dependency occurs, ~ 16 kOe. (Fig. 6). At H = 18.6 kOe. an appreciable increase in the magnetization below 20°K was observed whereas at H = 10.3 kOe. this rise was absent.

IV. Discussion of Results

As noted above substitution of Cu for Ni weakens exchange and lowers the transition temperatures. At $x = 2$ to 2.5 the lower transition temperature is lowered almost to helium temperatures and it appears that the second rise in the magnetization–field curve (Fig. 4) is associated with the phenomenon causing the lower transition temperature (see Fig. 6). Thus, the unusual field dependency results for $Y_2Ni_{15}Cu_2$ and $Y_2Ni_{14.5}Cu_{2.5}$ are not separate and additional aberrations requiring their own explanation.

The behavior of μ_{sat} with x shown in Fig. 3 seems quite remarkable. The rate of decline in μ_{sat} up to point A is consistent with the notion that Cu transfers its s electron to Ni upon entering the lattice, according to Assumption 1 above. This transfer is in accord with the conventional point of view (*9*, *10*) as regards Cu–Ni alloys although, as noted above, the dependence of μ_{sat} on composition is more nearly consistent with assumption 2 for binary systems. The transfer of charge is, moreover, in agreement with the point of view of d-transition metals put forth by Brewer (11), who regards the d orbitals as sinks for valence electrons. However, the transfer envisioned confers a positive charge on Cu and a negative charge on nickel. The charge transfer in moderation undoubtedly stabilizes the system but with increasing Cu and increasing potential difference further transfer becomes more difficult. With increasing Cu content, it appears that Cu retains a portion, perhaps 0.6, of its s electron. Thus, there is less transfer of charge per atom from Cu to nickel beyond point A in Fig. 3 and the decrease of μ_{sat} with x is less rapid. Looking at it another way, one can say that for x in the range of 2.55–4.5 the Fermi surface is rising so that Cu atoms now have s electrons. Thus, beyond point A, d electrons in nickel are of about the same energy as s electrons in

Cu and an equilibrium between the two traps for valence electrons can be imagined:

$$d \text{ electrons (Ni)} \rightleftarrows s \text{ electrons (Cu)}.$$

Application of a sufficiently high magnetic field should displace this equilibrium to the right since the magnetization of the system is thereby enhanced. It appears that the second rise in magnetization in Fig. 4 may arise in this way.

The equilibrium just described provides the basis of a mechanism, which although quite speculative, may explain the occurrence of the lower transition temperature for Y_2Ni_{17}. It seems clear that there is extensive transfer of charge from Y to Ni as this compound is formed resulting, as noted above, in considerable filling of the *d* orbitals of Ni and a sharp reduction in Ni moment. Nickel under these conditions has excess electrons in its core and its size is large in comparison with Ni in the elemental form. The 2–17 compound is a very close-packed structure with an average coordination number of $13\frac{1}{3}$. On cooling, this dense structure could compress the nickel, enlarged by excess electrons in its core, and force a release of bound *d* electrons into the conduction band. In other words, equilibrium similar to the one written above but involving localized (*d*) and delocalized electrons (*s*) for Ni could be displaced to the right by stresses imposed by cooling, giving rise to the enhanced moment. It appears that the lower transition temperature may originate in this way. Enlargement of the lattice by insertion of Cu (Fig. 2) would shift downward the temperature at which stresses force the aforementioned electronic rearrangement and this is indeed observed. The mechanism proposed here is entirely analogous to that accepted (*12*, *14*) for elemental Ce in which Ce^{3+} is partially transformed into Ce^{4+} upon cooling.

If the mechanism proposed is correct, the lower transition is due to a change in electronic configuration for Ni and the upper transition temperature is the true Curie temperature.

The aberrant behavior in Figs. 4 and 6 are not noted for samples with $x < 2$ or $\geqslant 3$. It appears that in the former case the *d* electrons are too low lying to be excited into s states by the field. For $x \geqslant 3$ the energy conditions are more nearly favorable but the magnetization of the Ni component is too weak to interact sufficiently strongly with the applied field. Only for *x* between 2 and 2.5 are conditions of moment and relative energy favorable so that the equilibrium can be shifted by the field.

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