sistivity decrease is probably due to the rearrangement of the dislocation network. Recrystallization occurs well above the stage IV recovery region in platinum and nickel.

#### **V. CONCLUSIONS**

1. Stage IV recovery in platinum is due to the migration of single vacancies.

2. The natures of the recoveries after electron irradiation in platinum and after deformation of nickel in stage IV region are very similar.

3. We suggest that the recovery mechanism is predominantly the diffusion of vacancies to inexhaustible sinks with concurrent trapping and releasing of vacancies by impurities.

4. Small concentrations of impurities with binding energies of the order of 0.8 eV are effective in delaying the recovery.

5. This suggests that the stage IV recovery in platinum and nickel, and possibly also in other metals, might be substantially affected by the introduction of selective impurities of low concentration.

### ACKNOWLEDGMENT

It is a pleasure to acknowledge the assistance of W. Goeppinger in the experimental part of this work.

PHYSICAL REVIEW

VOLUME 147, NUMBER 2

15 JULY 1966

# Magnetic Properties of Solid Solutions of the Heavy Rare Earths with Each Other

R. M. BOZORTH AND R. J. GAMBINO IBM Watson Research Center, Yorktown Heights, New York (Received 28 February 1966)

The Curie and Néel points, and other critical points, of alloys of heavy rare earth elements with each other have been determined for 14 binary alloy systems. To a good approximation the Néel points of all of the alloys vary linearly with the  $\frac{2}{3}$  power of the average de Gennes factor,  $J(J+1)(g-1)^2$ , as previously known. The Curie points, however, are definitely characteristic of the alloy system, each system showing a different dependence on concentration. The properties of each system are discussed, and related when possible to the transformations found in the elements and to atomic processes. Special effects are noted when the average 4f electron concentration lies between 10 (Ho) and 11 (Er), where the Stevens factor changes sign. Magnetization processes in several alloys are interpreted according to the model of Kitano and Nagamiya.

# INTRODUCTION

**P**REVIOUS work<sup>1-3</sup> has shown that the Néel points  $T_{\rm N}$  of the bosons and the bosons are shown that the Néel points  $T_N$  of the heavy rare earths and their alloys with each other can now be predicted; that is,  $T_N$  is closely proportional to the  $\frac{2}{3}$  power of the average de Gennes factor<sup>4</sup> of the material; this is amply confirmed in the present work though some systematic deviations can be detected. The Curie points, however, are distinctly characteristic of each alloy system. We have examined the binary systems in the range of elements Gd to Lu, omitting those with Yb, which do not form continuous solid solutions, and those with Tb, which have been studied by Child et al.<sup>5,6</sup> A partial understanding is acquired of the diverse behaviors of the Curie points and other transformations of the individual systems, as discussed below under each system.

## PREPARATION

The rare earth elements were obtained as 99.9% purity grade ingot or sponge, and all had been distilled except thulium. Alloys were prepared by argon arc melting using a nonconsumable tungsten electrode and a water-cooled copper hearth. The button ingots were turned over and remelted a minumum of five times to insure mixing. In all of the alloys except those containing Tm the weight loss on melting was less than 3%. The weight loss of the Tm alloys was much higher, some to 20%; these compositions were corrected assuming the loss to be all Tm. The samples were annealed in tantalum envelopes in quartz tubes at 1050°C (except those containing Tm which were annealed at  $850^{\circ}C$ ) for 16 to 20 hr and furnace cooled. X ray, microhardness, and metallographic examination showed all used alloys to be homogeneous solid solutions.

Single crystals of selected alloy compositions were

<sup>&</sup>lt;sup>1</sup>S. Weinstein, R. S. Craig, and W. E. Wallace, J. Appl. Phys. 34, 1354 (1963). <sup>2</sup> W. C. Koehler, E. O. Wollan, H. R. Child, and J. W. Cable,

<sup>&</sup>lt;sup>4</sup> W. C. Koenler, E. O. Wollan, H. K. Child, and J. W. Cable, *Third Rare Earth Conference* (Gordon and Breach, Science Publishers, Inc., New York, 1964), p. 199.
<sup>3</sup> Reviewed by W. C. Koehler, J. Appl. Phys. 36, 1079 (1965).
<sup>4</sup> P. G. de Gennes, Compt. Rend. 247, 1836 (1958).
<sup>5</sup> W. C. Koehler, H. R. Child, E. O. Wollan, and J. W. Cable, J. Appl. Phys. 34, 1335 (1963).
<sup>6</sup> H. R. Child, thesis, University of Tennessee, 1965 (unpublished)

published).

grown by the method described by Nigh.7 The arcmelted button ingots of about 10 g weight were supported by Ta and annealed by induction heating in flowing argon in a cold-walled quartz tube furnace. Annealing for 16 hr at 150°C below the melting point of the alloy was usually sufficient to produce an ingot consisting of two or three large grains.

## MEASUREMENTS

The measurements were made with the pendulum magnetometer previously described,<sup>8</sup> modified so that a full bridge of strain gauges of gauge factor 5 is mounted on the supporting phosphor bronze strip. Readings of the current (to 500 mA) that balances the moment of the specimen are normally made to 0.1 mA, corresponding to a moment of 0.003 cgs unit, but duplication of readings corresponds often to several times this value. The specimen was placed at the center of the coil attached to the bottom of the pendulum, in a Dewar of 1.2 in. i.d., and this was held in the 1.6-in. gap of an electromagnet producing fields to 25.8 kOe and gradients  $(dH/dx \perp H)$  to about 800 Oe/cm. Temperatures were from 1.25 to 300°K. A carbon resistor in contact with the specimen was used for temperatures to 77°K, a Au-Co versus Cu thermocouple above this temperature. The specimen could be immersed in liquid He, Ne, or N<sub>2</sub> if desired, without interfering with the measurement of moment.

### CRITERIA FOR CRITICAL POINTS

Because the temperature at which ferromagnetic properties appear in the rare-earths on cooling is



FIG. 1. Illustration of the method most used for determining the Curie point-the temperature of inflection point of the versus T curve extrapolated to H=0.



FIG. 2. Slope of  $\sigma$  versus T curve, using data of Fig. 1.

dependent on the applied field, the usual high-field methods cannot be used for determination of the Curie point  $(T_c)$ , the temperature at which spontaneous magnetization appears in zero field. In earlier work<sup>9</sup> we noted the critical field,  $(H_{cr})$  at which the linear magnetization curve, characteristic of the helical structure existing above  $T_c$ , changed to the nonlinear curve characteristic of ferromagnetism, and then extrapolated the  $H_{\rm cr}$  versus T curve to  $H_{\rm cr}=0$ . In later work<sup>10</sup> we have plotted the curve of moment  $(\sigma_m \text{ per mole})$  versus T for relatively low values of H (0.5 to 4 kOe), noting the temperatures of the points of inflection for each value of H and extrapolating these temperatures against H to H=0. This method was found to give the same values of  $T_c$  as those determined by the former method for a number of elements and alloys. It is also in agreement with simple molecularfield theory, and accordingly we now use this method almost exclusively. The existence of ferromagnetic properties at low temperatures is always tested by measuring over a range in field strength of from 1 to 25 kOe at 4.2°K or below.

Some precision may be necessary to determine the point of inflection. Usually this can be determined by eye (see Fig. 1) but a more objective result can be obtained by calculating  $\Delta \sigma_m/T$  for adjacent points and plotting this slope versus T(see Fig. 2). Both  $\sigma_m$  and T can be measured to 4 figures on relative scales,  $\Delta \sigma_m$ and  $\Delta T$  to 3 figures, though absolute accuracies are less. The peak in  $d\sigma_m/dT$  can be established at considerably less than one degree in favorable cases, sometimes, however, with an error of 2°K or more, especially at the higher temperatures.

The Néel point  $(T_N)$  was taken as the point of maximum  $\sigma_m$  in the familiar cusp-formed curve, also extrapolated to H = 0 from measurements made usually at

<sup>&</sup>lt;sup>7</sup> H. E. Nigh, J. Appl. Phys. 34, 3323 (1963).

<sup>&</sup>lt;sup>8</sup> R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. 103, 572 (1956).

<sup>&</sup>lt;sup>9</sup> R. M. Bozorth and J. C. Suits, J. Appl. Phys. 35, 1039 (1964).

 <sup>&</sup>lt;sup>10</sup> R. M. Bozorth and R. J. Gambino, in *Proceedings of the Inter-national Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1965), p. 263.



FIG. 3. Curie and Néel points of two Tm-Lu alloys of compositions shown. Note "approach" to Curie point of  $Tm_{0.53}$  Lu<sub>0.47</sub> at low temperatures.

H=1 and 2 kOe. In this case "Néel point" does not imply strict antiferromagnetic ordering of neighboring atoms but the helical ordering determined by neutron diffraction. Examples are shown in Fig. 3 where the point of inflection at  $T_c=11^\circ$  is also evident in the upper curve.

Another method of determination of  $T_c$  is illustrated in Fig. 4. When  $T > T_c$  the material becomes ferromagnetic when H is greater than a critical value  $H_{cr}$ . Although  $T_c$  is defined as the temperature at which spontaneous magnetization occurs in zero field, ferromagnetic properties are often observed above a critical field  $H_{\rm er}$  when  $T > T_c$ , and  $T = T_c$  when  $H_{\rm er}$  extrapolates to zero, as shown in Fig. 5. Also in this figure are shown illustrative data for the determination of  $T_N(H)$ for the same alloy. The quantities  $T_C$ ,  $H_{cr}$ ,  $T_N(H)$  can all be shown in the same figure, as in Fig. 5; and as discussed below, the position of other transformation temperatures can also be shown on this kind of a diagram. It may be noted that the form of the break at  $T_N(H)$  has a different character, depending on whether the field in which it is measured is above or below the maximum value of  $H_{\rm cr}$ .

In Fig. 5 the area of ferromagnetism (FM) is clearly



FIG. 4. Data for  $Gd_{1/8}$  Dy<sub>7/8</sub> showing critical fields and Néel points, and changes of magnetization in weak and strong fields near the Néel point.

defined at the lower temperatures shown; between  $175^{\circ}$  and  $193^{\circ}$ K  $(T_N)$ , when the  $H_{\rm er}$  line bends down, the behavior is more difficult to interpret. This transition region, marked R, appears to have some relation to the region in a normal ferromagnetic material just above  $T_c$ , in the presence of a high field which is able to accomplish a considerable amount of alignment and so simulate ferromagnetism. See also the discussion of Fig. 8 under Gd-Lu alloys. There is apparently no definite boundary between the areas FM and PM (paramagnetic) in high fields just as there is no boundary in a phase diagram of a fluid, between a liquid and a gas, above the critical pressure.

In some alloy systems the moments were measured to 25 kOe at helium temperatures. To avoid the disturbing effect of nonrandom crystal orientations in the specimen, it was cut in approximate cubic form, measured in each of the three mutually perpendicular directions, and the results averaged. Moments so



FIG. 5.  $T_C$ ,  $H_{cr}$ ,  $T_N$ , and  $T_N(H)$  (Néel point for  $H \neq 0$ ) for  $Gd_{0.125}$  Dy<sub>0.876</sub>, showing antiferromagnetic (AF) and ferromagnetic (FM) regions. For R see text.

determined are then found to be a smooth function of composition, as already shown for Gd-Dy and Ho-Er alloys.<sup>10</sup>

The magnetic fields noted in the figures are the applied fields, uncorrected for demagnetizing factor, unless otherwise stated.

#### RESULTS

A summary of the measurements of  $T_c$  and  $T_N$  is shown in Fig. 6. Data for some of the systems are also shown on a larger scale in later figures.

Néel points, plotted in Fig. 6 as open symbols, show here a considerable variation from one binary system to another. They become well coordinated, however, in Fig. 7 where they are plotted against the  $\frac{2}{3}$  power of the average value  $\tilde{G}$  of the de Gennes factors<sup>4</sup> G=J(J+1) $(g-1)^2$  for the rare earth atoms present:

$$\bar{G} = c_1 G_1 + c_2 G_2,$$
  
 $T_N = 46.7 \bar{G}^{2/3},$ 



FIG. 6. Summary of results for  $T_N$ ,  $T_c$ , and  $T_x$ . See also Figs. 9, 10, 16, and 19.

 $c_1$  and  $c_2$  being the atomic concentrations of the two components. The representative data of the figure are from our own experiments and those of the Oak Ridge group.<sup>3,6</sup> As shown by neutron diffraction,<sup>11</sup>  $T_N$  is the temperature below which each hexagonal plane is ferromagnetic but its magnetization is not parallel to its neighbors, the angle varying with temperature and field.

490

Recently Child and Koehler<sup>12</sup> have observed Néel



FIG. 7. Selected data for various systems, to show the empirical relation  $T_N \propto \bar{G}^{2/3}$ .

points considerably lower than those predicted by the relation given above, for Tb-Sc alloys.

Gd-Dy alloys. Originally this system was studied<sup>9</sup> to find the composition at which the spiral structure of Dy just disappeared. As Fig. 6 shows,  $T_N$  and  $T_C$ coincide at about 50 at.% and the intermediate spiral structure is absent in Gd-rich alloys. The Curie points were determined here by extrapolating the critical field to zero, as in Fig. 5 above.

The mechanism of the breakdown of the Dy-type anti-ferromagnetic structure by the application of fields greater than  $H_{cr}$  is now established as the "fanning" of the vectors, which lie in the basal plane, into those positions in the plane which are most nearly parallel to the field. The data of Fig. 4 show the onset of fanning, and the change with temperature of the susceptibility in low fields (with a maximum at  $T_N$ ). Figure 5 shows a decrease in  $H_{\rm cr}$  as T approaches  $T_N$ . This can be understood in terms of the model of Kitano and Nagamiya,13 for their theory indicates that here the heights of the  $T_N(H)$  and the  $H_{\rm er}$  curves should approach the ratio 2/1.

The moments at saturation,<sup>9</sup> as inferred from a plot versus 1/H, extrapolated from 25 kOe, show a change with composition from about 7 Bohr units at Gd to about 8 at Dy; the former is the theoretical gJ, the latter nearly  $gJ\pi/4=7.85$ , as previously observed<sup>14</sup> and as calculated for material in which the moment is confined to the c plane by high anisotropy forces but may be drawn into any orientation in the plane.

Gd-Ho alloys. Curie points drop rapidly with in-

<sup>&</sup>lt;sup>11</sup> W. C. Koehler, J. Appl. Phys. Suppl. **32**, 20 (1961). <sup>12</sup> H. R. Child and W. C. Koehler, J. Appl. Phys. (to be published).

<sup>&</sup>lt;sup>13</sup> Y. Kitano and T. Nagamiya, Progr. Theoret. Phys. (Kyoto)

<sup>31, 1 (1964).</sup> <sup>14</sup> D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev.

creasing Ho concentration above 40%, and below this concentration there is no evidence of a spiral structure. The  $T_c$  versus  $n_{4f}$  curve runs closely parallel to that for Gd-Dy alloys.

Gd-Er alloys. Here the spiral structure of Er, stable between  $T_c$  and  $T_N$ , disappears when the Gd concentration exceeds 50 at.%, as in the Gd-Dy system. The Curie points for larger concentrations of Er drop rapidly, at first linearly and then less rapidly when  $n_{4f}$  is near 10.5, then again rapidly toward pure Er. This departure from linearity is more marked in Ho-Er alloys and is discussed below.

Gd-Tm alloys. The Curie points lie above the line for Gd-Er alloys, as expected, and show the upward bulge near  $n_{4f} = 10.5$ . The Tm-rich alloys show a minimum below 5°K between 85 and 90 at.% Tm, and the 91.5 at.% alloy shows two Curie points, at 5 and 18°. The latter is due presumably to the formation of the Tmtype magnetic structure so that  $T_{c_2}$  approaches 25°K as Tm approaches 100%. See the detailed discussion of two Curie points under Er-Tm alloys.



FIG. 8. Diagram of critical points in the  $Gd_{0.5}$  Lu<sub>0.5</sub> alloy having a helical structure at H=0, T=0. In region AF helical structure obtains; in FM<sub>1</sub> magnetization "fans" and takes up fixed azi-muths around the hexagonal axis; in FM<sub>2</sub> the field destroys the fan structure and magnetization approaches saturation. Fields for  $H_{\rm cr}$  and  $H_x$  corrected for demagnetizing factor.

Gd-Lu alloys. The Néel points of these alloys follow closely the  $\bar{G}^{2/3}$  law, and this relation is valid also for  $T_c$  for Gd-rich alloys which show no antiferromagnetic phase. The Curie points drop rapidly from about 20 at.% Lu and ferromagnetism could not be established above 45 at.% Lu-the moments are presumably in a fixed antiferromagnetic spiral. In alloys with higher Lu contents, e.g., 50% (Fig. 8), apparently the anisotropy associated with the antiferromagnetic state prevents saturation in low fields, though in higher fields ferromagnetism occurs, as indicated by  $H_{cr}$  and  $T_x$ . It is suggested that in the area FM<sub>1</sub> the moments in the hexagonal planes have "fanned" because the field has overcome the exchange and crystal anisotropy in the plane, and in the area of FM<sub>2</sub> the field has overcome also the axial anisotropy. This is in general accord with the magnetization processes proposed by Kitano and Nagamiya<sup>13</sup> on theoretical grounds.

The ferromagnetic moments at  $4.2^{\circ}$  and 25 kOe show  $n_B/Gd$  to be greater than 7.0, in agreement with the





measurements of Nigh et al. on pure Gd15 and on Gd-Sc alloys.<sup>16</sup> Popplewell, Harris, and Tebble<sup>17</sup> have also observed an increase in  $\mu_{eff}/Gd$  over the theoretical value 7.9 and ascribe this to the effect of the conduction electrons, as proposed by Liu.<sup>18</sup>

Tb alloys Alloy systems of Tb with Dy, Ho, Er, Tm, and Lu have been investigated by Child, Koehler, Wollan, and Cable, <sup>6,19</sup> and their values of  $T_c$  and  $T_N$ are plotted with the summary for various systems in Figs. 6 and 7. Values of  $T_N$  all follow the empirical  $\frac{2}{3}$ power law. Alloys having an electron concentration of  $n_{4f}$  less than 10 have  $T_c$ 's near our curve for Gd-Dy, and few values are reported for higher concentrations.

Dy-Ho alloys. Only one alloy of this system was prepared. Since the Curie point lies almost midway between those of Dy and Ho, and since it is close to the value reported by Child,6 no further experiments were made.

Dy-Er alloys. The Curie points (Fig. 9; not included in Fig. 6) show a maximum near  $n_{4f} = 10.5$ , as in the Ho-Er alloys to be discussed below. There is a break in



<sup>15</sup> H. E. Nigh, S. Legvold, and F. H. Spedding, Phys. Rev. **132**, 1092 (1963).

<sup>16</sup> H. E. Nigh, S. Legvold, F. H. Spedding, and B. J. Beaudry, J. Chem. Phys. 41, 3799 (1964).
 <sup>17</sup> J. Popplewell, A. M. Harris, and R. S. Tebble, Proc. Phys.

<sup>14</sup> J. Poppiewen, A. M. Harns, and K. S. LEDDE, Proc. Phys.
 Soc. (London) 85, 346 (1965).
 <sup>18</sup> S. H. Liu, Phys. Rev. 123, 470 (1961); see also J. Kondo,
 Progr. Theoret. Phys. (Kyoto) 28, 846 (1962).
 <sup>19</sup> H. R. Child, W. C. Koehler, O. Wollan, and J. W. Cable,

Bull. Am. Phys. Soc. 9, 213 (1964).

the curve just above  $n_{4f}=10$ , presumably when the structure changes abruptly from the Dy-type, with an easy direction in the hexagonal plane, to the Er-type with the easy direction parallel to **c**.

Dy-Tm alloys. Tc's have a marked minimum of 7°K near  $n_{4f}=10$ , not far from the critical concentration corresponding to  $n_{4f}=10.5$ , to be discussed especially for the Ho-Er alloys.

Ho-Er alloys. Although the Néel points show a smoothly decreasing trend with increasing Er content, there is a high maximum in the Curie point curve at  $T_c=35^\circ$ , almost twice the Curie points of the two elements (Fig. 10). These two elements have crystal anisotropies of different character, Ho having a direction of easy magnetization in the hexagonal plane,<sup>20</sup> Er one parallel to the hexagonal axis.<sup>21</sup> They also have



FIG. 11. Magnetization of single crystal sphere of Ho<sub>0.5</sub> Er<sub>0.5</sub>.

magnetostriction of opposite sign.<sup>22</sup> These properties are associated with the change of sign of the Stevens factor<sup>23</sup>  $\alpha$  which is negative in the first half of the heavy rare earths (Tb-Ho) and positive in the second half (Er-Tm). The change in sign of  $\alpha$  has also an effect on the Curie points of the Gd-Er alloys, as shown by the bump in the  $T_C$  versus  $n_{4f}$  curve of Fig. 6. Discussion of the relation between  $T_C$  and the crystalline fields, by Freiser, has already appeared.<sup>10</sup>

To investigate further the behavior of this system a single crystal was prepared of the 50 at.% alloy and this was studied by Shirane and Pickart<sup>24</sup> by neutron diffraction; its anisotropy<sup>25</sup> and magnetostriction<sup>26</sup> are

<sup>23</sup> K. W. H. Stevens, Proc. Phys. Soc. 65, 209 (1952).

<sup>25</sup> B. A. Calhoun and R. M. Bozorth (private communication).



FIG. 12. Critical points for Er:  $T_c=19^\circ$ ,  $T_{x2}=28^\circ$ ,  $T_{x1}=54^\circ$ ,  $(T_N=84^\circ \text{ not shown})$  and effect of small addition of Ho.

under investigation. The neutron diffraction results show that in the ferromagnetic state at low temperatures the magnetic vectors form a cone spiral structure in which both Ho and Er atoms are inclined at 53° to the basal plane, as compared to 80° and 29° for the elements Ho and Er,3 respectively. This behavior contrasts with that of the Dy-Er alloys in which a definite discontinuity in the  $T_c$  versus composition curve is observed. Magnetic measurements (Fig. 11) made parallel and perpendicular to the c axis, on a sphere cut from the same single crystal, are in excellent agreement with the neutron results; magnetization parallel to the axis increases rapidly with increasing field until  $n_B = 9.5$  $\cos \theta$ , where  $\theta$  is the cone angle of 52°, while that perpendicular to the axis breaks down the helical structure to produce fanning only when 20 kOe have



FIG. 13. Moments of Tm as dependent on temperature, showing points of inflection  $(T_c)$  and transformation  $(T_x)$ .  $T_x$  was repeatedly observed in different specimens at 33° in fields of 1, 2, and 10 kOe.

 <sup>&</sup>lt;sup>20</sup> D. L. Strandburg, S. Legvold, and F. H. Spedding, Phys. Rev. 127, 2046 (1962).
 <sup>21</sup> R. W. Green, S. Legvold, and F. H. Spedding, Phys. Rev.

<sup>&</sup>lt;sup>42</sup> R. W. Green, S. Legvold, and F. H. Spedding, Phys. Rev 122, 827 (1961).

<sup>&</sup>lt;sup>22</sup> T. Tsuya, A. E. Clark, and R. M. Bozorth, in *Proceedings of the International Conference on Magnetism*, Notlingham, 1964 (The Institute of Physics and The Physical Society, London, 1965), p. 250.

<sup>&</sup>lt;sup>24</sup> G. Shirane and S. J. Pickart, J. Appl. Phys. (to be published).

<sup>&</sup>lt;sup>26</sup> A. B. Clark and J. J. Rhyne (private communication).





been applied—it then attains suddenly the magnitude  $n_B = 9.5 \sin \theta$  with  $\theta = 55^{\circ}$ . These angles are in good agreement with the neutron results which gave  $\theta = 53^{\circ}$ .

The effect of a small addition of Ho to Er (Fig. 12) is discussed under Er-Tm alloys.

Ho-Tm alloys. As with the Ho-Er alloys, the Curie points show a maximum at the 4f electron concentration of  $n_{4f} \approx 11$ , when  $T_C$  is almost equal to that of Er. The magnetic structures of Ho and Tm are distinctly different, but it is unknown at what composition the alloy changes from one structure to the other; presumably this occurs between  $n_{4f} = 10.4$  and 11.0.

Er-Tm alloys. Measurements were made on the elements as well as the alloys of this system. In Er we found  $T_c = 19^\circ$  and two other transformations below  $T_N(84^\circ)$  at, respectively,  $T_x = 28$  and  $54^\circ K$  (Fig. 12). The latter had already been identified<sup>3</sup> as a change in magnetic structure; the one at 28° is new as far as we are aware.

Several specimens of Tm were measured, each prepared in a different way. They all showed a sharp break in the  $\sigma$  versus T curve at  $T_x = 32(33^\circ \text{ for } 2 \text{ kOe})$ , above the point of inflection at  $T_e = 25^{\circ}$  (Fig. 13). This break appeared at the same temperature when fields of 1, 2, and 10 kOe were used. Data for  $\sigma_m$ , and  $\Delta \sigma_m / \Delta T$ for neighboring points, are given in Figs. 13 and 14. Neutron-diffraction data<sup>27</sup> have already indicated a change in magnetic structure at 33°.

FIG. 15. Hysteresis loops for Tm speci-mens of different tantalum contents.



27 W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, J. Phys. Soc. Japan 17, Suppl. BIII, 32 (1962).



FIG. 16. Various critical points observed in Er-Tm and related alloys:  $T_N$ ,  $T_x$ , and two Curie points,  $T_{C1}$  and  $T_{C2}$ .

The value of  $T_c = 25^\circ$  is in fair agreement with the value 22° previously reported,28 based on the disappearance of hysteresis. Hysteresis loops at 4.2° (Fig. 15) show a coercive force of about 2 kOe in material both as received (analyzed by ion spectroscopy as containing 0.6 at.% Ta and 0.4 at.% O) and in the same material distilled (0.0 at.% Ta, 0.4 at.% O). In the undistilled material the loop widens and additional hysteresis appears above 10 kOe. In further measurements in high fields  $\sigma_m$  of the distilled material was found to increase rapidly at about 30 kOe, and at 50 kOe the magnetization was about 2.0 Bohr magnetons. This rapid rise is consistent with the results of Henry<sup>29</sup> who observed 3.4 Bohr magnetons at 70 kOe; this is presumably due<sup>28</sup> to the averaging of the theoretical 7 Bohr magnetons in polycrystalline material with a very high axial anisotropy. The apparent approach to a saturation of 0.5 Bohr magneton in polycrystalline material in the lower fields is in agreement with the 4343 structure



FIG. 17. Determination of the two Curie points in an Er-Tm alloy, and onset of second ferromagnetic phase at 22°.

<sup>&</sup>lt;sup>28</sup> D. D. Davis and R. M. Bozorth, Phys. Rev. 118, 1543 (1960). See also the mention of 22°K by L. D. Jennings, Emma Hill, and F. H. Spedding, J. Chem. Phys. 34, 2082 (1961), and the more recent article by F. J. Jelinek, E. D. Hill, and B. C. Gerstein, J. Phys. Chem. Solids 26, 1475 (1965). <sup>29</sup> W. Henry, J. Appl. Phys. 31, 323S (1960).

determined by Koehler *et al.*<sup>30</sup> by neutron diffraction, and the increase in higher fields is apparently due to the breakdown of this structure.

Addition of Tm to Er (Fig. 16) at first lowers the Curie point rapidly toward a value of  $T_{C1}$  of 0°K at 20 to 30 at.% Tm (at 23 at.% the material appears to be ferromagnetic or "almost" so below 3°K). At the same time ferromagnetism appears again at higher temperatures (see Fig. 17) over the range of about 7 to 25 at.% Tm, and the high-temperature Curie points  $(T_{C2})$  continue to pure Tm, as indicated in Fig. 16.

This figure shows also that the well-known transition<sup>3</sup> at 54° in pure Er is lowered by additions of Tm to join the  $T_{C2}$  at its low Tm-concentration end. The same line is continued to lower concentrations of 4f electrons by additions of Ho. The line for  $T_{C2}$  is also continued beyond pure Tm by additions of Lu. The line for  $T_{C1}$  is continued for lower 4f electron concentrations by a small addition of Gd, but the path diverges for additions of Ho.

*Er-Lu alloys.* The alloys which we have studied appear to have a critical field below which the magnetization is almost linear and above which the mag-



FIG. 18. Change in structure of  $Er_{4}Lu$ , with applied field and approach to saturation. Note hysteresis related to the two structures.

<sup>30</sup> W. C. Koehler, J. W. Cable, E. O. Wollan, and M. K. Wilkinson, Phys. Rev. **126**, 1672 (1962).



FIG. 19. Loss of ferromagnetism by addition of Lu to Tm, and adherence of  $T_N$  to empirical relation.

netization increases rapidly. At 4.2° marked hysteresis is present in the alloys  $\text{Er}_{0.95}$  Lu<sub>0.05</sub> and  $\text{Er}_{0.98}$  Lu<sub>0.02</sub> at H=0, after applying a higher field. Moments were measured at 1 and 2 kOe after applying 25 kOe, and a point of inflection was noted for the latter alloy at 10°K, for the former alloy at 13°K. No inflection could be found for the  $\text{Er}_{0.9}$  Lu<sub>0.1</sub> alloy, but hysteresis is still observed at 4.2° in low fields after application of a high field in the alloy  $\text{Er}_{0.75}$  Lu<sub>0.25</sub> (Fig. 18).

*Tm-Lu alloys.* The Curie points drop rapidly with increasing Lu and extrapolate to zero at about 37 at.% Lu (Fig. 19). Néel points of 5 alloys follow the  $\frac{2}{3}$  power law accurately but with a proportionality constant of 51.5, somewhat higher than the constant 46.7 used for the straight line of Fig. 7. The data for Tm<sub>0.53</sub> Lu<sub>0.47</sub> indicate that ferromagnetism is approached at low temperatures, and the position of the line for  $T_c$  in Fig. 19 is in agreement with this.

## **ACKNOWLEDGMENTS**

We are glad to acknowledge the help of J. J. Cuomo and H. G. Schaefer in the preparation and examination of the alloys, and of J. W. Mitchell with the measurements. Benefit has been derived from various conversations with B. A. Calhoun, A. B. Clark, and J. J. Rhyne.

494