the observed maximum value at 0.7°K, 1.0 cal/mole °K$\equiv 0.50R$, is due partly to such additional contributions as the low-temperature "tail" of the cooperative peak at 3.18°K, it would appear that f is not much larger than $\frac{1}{2}$. Whether f could be as small as $\frac{1}{3}$ is not clear since this would require the non-Schottky contributions to C_p at 0.7°K to be rather large.

Unfortunately, it appears difficult to reconcile $\frac{1}{3}< f\leq\frac{1}{2}$ with observations that the saturation moment of $Mn(CH_3COO)_2\cdot 4H_2O$ near 1°K is $(5/3)\mu_B/(Mn^{++}$ ion). According to preliminary x-ray studies of the structure of this salt,[14] there are 12 Mn^{++} ions per unit cell distributed over two groups of inequivalent sites α and β containing, respectively, four and eight ions. Note that a dominant antiferromagnetic interaction $J_{\alpha\beta}$ could lead to a simple collinear ferrimagnetism and the observed saturation moment without, however, giving a Schottky anomaly according to the suggested mechanism. On the other hand, a strong ferromagnetic interaction $J_{\alpha\alpha}$, negligible $J_{\beta\beta}$, and weak $J_{\alpha\beta}$, could give the observed saturation moment and a Schottky anomaly, but with $f=\frac{2}{3}$. Such an f value would cause $C_p(\max)$ to be at least $0.57R$, which is larger than the observed magnitude and, thus, unlikely.

Other simple collinear spin arrangements, constructed so as to make $f=\frac{1}{2}$, appear artificial in the light of the limited structural evidence available. Presumably, noncollinear models could be constructed satisfying simultaneously all the empirical constraints discussed above. We prefer not to attempt this, however, until the structure of $Mn(CH_3COO)_2\cdot 4H_2O$ has been definitely established.

[14] R. Baughman (private communication); H. Iwasaki (private communication to I. Tsujikawa cited in Ref. 2).

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Neutron Diffraction and Susceptibility Study of Dilute La–Rare-Earth Alloys*

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Neutron diffraction and susceptibility data are reported for dilute solutions of rare-earth impurity in a La host. At magnetic impurity levels of 10 and 20 at.%, the La-Tb alloys show a broad neutron diffraction peak characteristic of short-range order at 7° from the forward direction. At a magnetic impurity level of 5 at.%, this short-range order peak is absent, and the magnetic scattering in the ordered state is the same as the scattering in the paramagnetic state. Within experimental error, the Tb ions maintain their full moment and there is no change in the scattering which can be associated with spin compensation by the conduction electrons. Susceptibility data for these alloys are in many respects similar to results reported for Cu-Mn alloys, but there are important quantitative differences. Pure double-hcp La shows a nearly temperature-independent susceptibility in fair agreement with that predicted from the specific-heat density of states.

INTRODUCTION

DILUTE solutions of magnetic impurity in a nonmagnetic host can show a variety of phenomena including giant susceptibilities,[1] specific heat anomalies,[2,3] resistance minima,[4] and several aspects of the Kondo state.[5,6] Presumably, these effects all arise from magnetic-impurity scattering of the conduction electrons. Extensive investigations[4] have been made for the 3*d* transition element impurities in Cu, Ag, and Au, and more recently Sugawara and colloborators[7] have undertaken a systematic study of the 4*f* rare-earth impurities in La and Y. Many of the same phenomena occur in both systems, although there are differences associated with the highly localized character of the moment in the 4*f* series.

At high magnetic-impurity concentration, the rare-earth group shows many different long-range-ordered structures,[8] including ferromagnetism, helical phases, and other more complicated structures. As the concentration of magnetic moment decreases, however, the range of order decreases and the long-range character disappears. In the case of Y-Tb alloys,[9] a well-defined helical structure persists over the entire range from

* Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Contribution No. 2319.

[1] R. P. Guertin, J. E. Crow, and R. D. Parks, Phys. Rev. Letters **16**, 1095 (1966).

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[3] N. E. Phillips and B. T. Matthias, Phys. Rev. **121**, 105 (1961).

[4] G. J. van den Berg, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio,* edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965).

[5] J. Kondo, Progr. Theoret. Physics (Kyoto) **33**, 575 (1965).

[6] J. Kondo, Progr. Theoret. Physics (Kyoto) **32**, 37 (1965).

[7] T. Sugawara and H. Eguchi, J. Phys. Soc. Japan **21**, 725 (1966).

[8] W. C. Koehler, J. Appl. Phys. **36**, 1078 (1965).

[9] H. R. Childs, W. C. Koehler, E. O. Wollan, and J. W. Cable, Phys. Rev. **138**, A1655 (1965).

pure Tb to $Y_{95}Tb_5$ with an ordering temperature of 25°K for 5 at.% Tb. In the case of La-Tb alloys, however, the ordering temperature is much lower (5.7°K for 5 at.% Tb concentration) and short-range order sets in at a higher Tb concentration than in the Y-Tb alloys.

La is of special interest as a host material for the study of the magnetic ordering process because it also shows superconductivity and there is the possibility of studying superconductivity in the presence of magnetic order.[3,10] The effect of spin-flip scattering on the superconductivity when the magnetic ions are paramagnetic is fairly well understood[11,12] but very little is known about the magnetically ordered state or the mechanism for ordering. The primary sources of information in this field have been specific heat, susceptibility, Mössbauer[13] and NMR[14] data. Specific-heat measurements have shown that there is an entropy change to be associated with full ordering of the spins[3,10] and magnetization measurements[10] show that the ordered state has a moment much smaller than the Curie-Weiss value, but, no experiments have been shown details of the order.

A statistical model for these systems, which was proposed by Klein and Brout and by Marshall,[15] explains many aspects of these results, and this theory has recently received support from the specific-heat measurements on Zn-Mn alloy by Martin.[16] The susceptibility measurements in the 4*f* system, however, show substantial disagreement,[1] and although many aspects of this theory are very attractive, it appears that other factors must be included for a complete description.

We report here a series of magnetization, differential susceptibility, and neutron-diffraction results for dilute La–rare-earth alloys. In the early stages of this work Gd was chosen as the magnetic impurity because it has no orbital contribution to the moment and it was hoped that the theory would be simpler for a spin-only system. As it became clear that neutron diffraction studies were desirable, we switched to Tb as the magnetic impurity because Gd has such a high-absorption cross section for thermal neutrons.

TABLE I. Analysis of pure La in ppm by weight.

C	40
N	10
O	60
H	5
Ni	20
Fe	30
Mg	5
Si	60
Ca	10
F	150

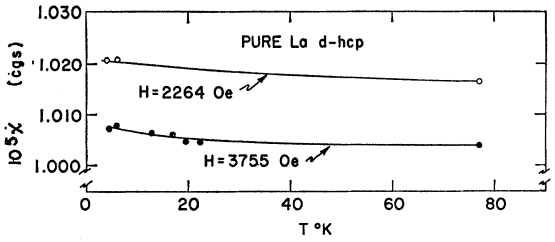

FIG. 1. The susceptibility of pure La.

SUSCEPTIBILITY OF PURE La

Magnetization measurements for double-hcp La were all performed with a sample motion apparatus that was essentially the same as that used in a study of superconducting Nb.[17] The sample was cut from another specimen whose specific heat was reported earlier[18] and it was shaped with a jeweler's saw and emery cloth into an ellipsoid with a demagnetizing factor of 1.65. Mechanical strain tends to promote the double-hcp phase so the cutting process will not increase the amount of fcc modification present unless the sample is heated above 175°C. After a final polish with No. 1 emery paper, a surface layer approximately 0.005 in. thick was removed by electropolishing. No chemical analysis was made after the measurement but an analysis of the base La material shows the impurities given in Table I. The total rare-earth impurity in these La samples is typically less than 30 ppm but this particular sample has not been analyzed.

Figure 1 shows that the susceptibility of pure La is nearly independent of both temperature and magnetic field. As the temperature decreases from 78 to 4.2°K, χ changes by only 0.3%. As the magnetic field increases from 2264 to 3755 Oe, χ decreases by about 1.2%. The magnitude of the susceptibility of about 1.0×10^5 cgs units, where B, H, and M are measured in emu/cm^2, is in fair agreement with previous experiments[19,20] and is about 15% lower than the value calculated for the Pauli spin susceptibility, using the specific-heat density of states of 2.0 (states/eV) molecule. If an additional correction is made for the electron-phonon coupling by $\chi=\chi_P/[1+N(0)V]$, where $N(0)V=0.24$ is deter-

[10] D. K. Finnemore, D. C. Hopkins, and P. R. Palmer, Phys. Rev. Letters **15**, 891 (1965).
[11] W. R. Decker and D. K. Finnemore, Phys. Rev. **172**, 430 (1968).
[12] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 178 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].
[13] T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. 138 A467 (1965).
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[15] M. W. Klein, Phys. Rev. Letters **16**, 90 (1966); Phys. Rev. **141**, 489 (1966); M. W. Klein and R. Brout, *ibid.* **132**, 2412 (1963); M. Marshall, *ibid.* **118**, 1520 (1960).
[16] D. L. Martin, Phys. Rev. **167**, 640 (1968).
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[18] D. K. Finnemore, D. L. Johnson, J. E. Ostenson, F. H. Spedding, and B. J. Beaudry, Phys. Rev. **137**, A550 (1965).
[19] F. H. Spedding, S. Legvold, A. H. Daane, and L. D. Jennings, in *Progress in Low Temperature Physics* (North-Holland Publishing Co., Amsterdam, 1957) Vol. II; J. M. Lock, Proc. Phys. Soc. (London) B**70**, 566 (1957).
[20] W. E. Gardner (private communication).

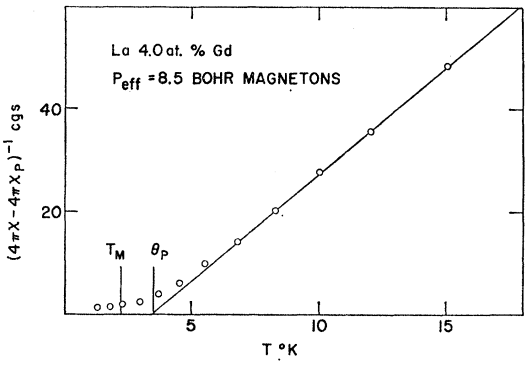

FIG. 2. The Curie-Weiss behavior of a La 4.0 at.% Gd sample. The effective moment was determined from the slope of the curve.

mined from the superconducting properties,[21] the calculated value of 0.96×10^{-5} cgs is about 7% below the measured value. At present, no theory is adequate to calculate these parameters in a complicated metal like La, but it is encouraging that the simple theories are reasonably close.

MAGNETIZATION OF La-Gd ALLOYS

All the measurements for Gd concentrations up to 0.8 at.% Gd were made on materials cut from samples previously used for specific-heat measurements.[18] For higher concentrations, new alloys were prepared by the same method.

At high temperatures the alloys obey a Curie-Weiss law with $(4\pi\chi)^{-1}$ versus T plots similar to that of Fig. 2. The susceptibility of pure La, χ_p, has been subtracted from the total so that the effect of the Gd is shown more clearly. The paramagnetic Curie temperature θ_p is positive for all the Gd alloys and it increases linearly with Gd concentration at about 1°K/at.% Gd as shown in Fig. 3. The effective moment/Gd ion p_{eff} as determined from the paramagnetic Curie constant is very near the free-ion value of 7.94 Bohr magnetons (μ_B) at low concentration as shown

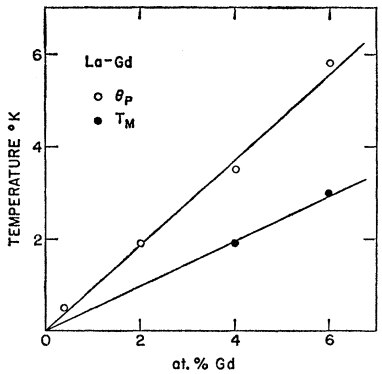

FIG. 3. The concentration dependence of the paramagnetic Curie temperature θ_p and the maximum in the susceptibility T_M.

[21] D. L. Johnson and D. K. Finnemore, Phys. Rev. **158**, 376 (1967).

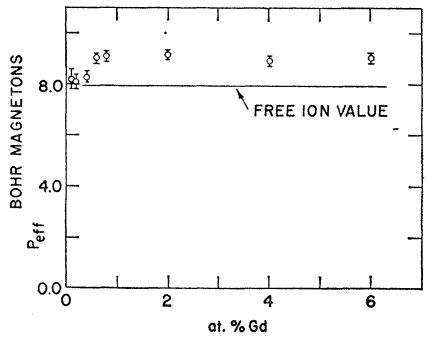

FIG. 4. Effective moment for Gd ions in a La host.

in Fig. 4 but for concentrations about 1 at.% Gd, p_{eff} rises to about $8.5\mu_B$. Presumably, the extra half Bohr magneton is caused by a polarization of the conduction electrons parallel to the Gd moment.

In many ways the susceptibility of these alloys is similar to the $La_{1-x}Gd_x$ in reports related by Guertin *et al.*[1] The data, illustrated in Fig. 5, rise well above the Curie law susceptibility and go through a distinct maximum at a temperature T_M which increases with increasing Gd content. As shown in Fig. 3, T_M is approximately $\frac{1}{2}$ the value of θ_p and it is in good agreement with the ordering temperatures given by Hein *et al.*[22] At the maximum, the magnitude of χ is much larger than that predicted from the Brillouin function. For example, the 6 at.% Gd specimen has a susceptibility that is 12 times the Curie-law value as shown by the dashed line of Fig. 5. As the Gd concentration increases, there is a distinct rise in the magnitude of the susceptibility at T_M, contrary to the predictions of Klein.[15] Liu,[23] however, has shown that a modification of the theory to include molecular field effects can give rise to susceptibility curves qualitatively similar to those of Fig. 5.

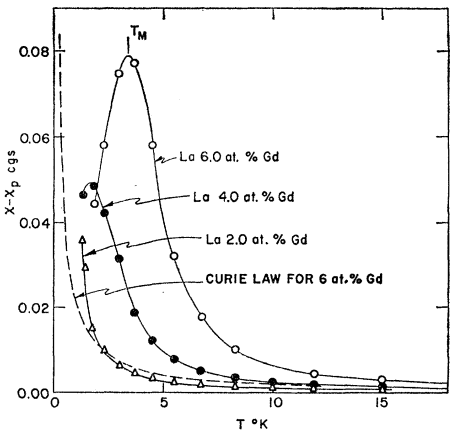

FIG. 5. Giant magnetic susceptibilities for the La-Gd system. At the peak, the susceptibilities are much larger than the Curie law.

[22] R. A. Hein, R. L. Falge, B. T. Matthias, and E. Corenzwit, Phys. Rev. Letters **2**, 500 (1959).

[23] S. H. Liu, Phys. Rev. **157**, 411 (1967).

An important feature of these data is that a rather small external field can radically depress the susceptibility as shown by Fig. 6. A field of only 200 Oe will depress χ by a factor of 2 even though the magnetic energy $\mu \cdot B$ is only about 3% of the characteristic ordering energy kT_M. At present there is no theory that predicts such a radical drop.

NEUTRON SCATTERING IN POLYCRYSTALS

One of the goals in this work was to establish the magnetic-impurity concentration at which the long-range order breaks down and short-range order becomes important. To this end, neutron patterns have been taken for polycrystalline La 20 at.% Tb and La 10 at.% Tb samples that were approximately $\frac{3}{8}$ in. thick. The apparatus consisted of a double axis Mitsubishi diffractometer using monochromatic neutrons with a wave length of 1.158 Å. Samples were mounted in a two-chamber He^4 cryostat that allowed the temperature to be continuously varied from 1.3 to 78°K. Above 20°K, a copper constantan thermocouple was used as the primary thermometer and below this temperature a Speer carbon resistor, which had been calibrated against a constant volume-gas thermometer,[18] was used.

Samples were prepared by arc melting a finger of the alloy several times to ensure homogeneity. The sample was then sealed in a Ta envelope to prevent oxidation, and a room-temperature neutron spectrum was run in the "as cast" state. Line intensities varied by as much as 10% as the sample orientation was changed, so there was a small amount of preferred orientation in the sample. This factor limits the accuracy of the measurement. In the "as cast" state the (102) double-hcp line was about 4 times as intense as the (200) fcc line, so there were substantial portions of both phases present. An anneal at 175°C for a week produced very

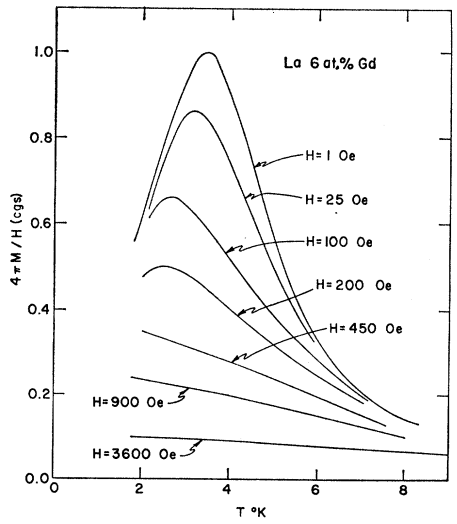

FIG. 6. The magnetic field dependence of the susceptibility. Very small applied fields produce large changes in the peak susceptibility.

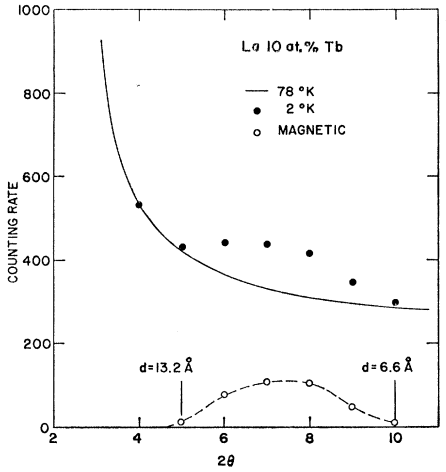

FIG. 7. Neutron-diffraction powder pattern in the forward direction. The open circles show the difference between the 2 and the 78°K data.

little change in the relative intensities of these peaks, but an anneal at 400°C for 16 h decreased the (200) fcc line intensity by a factor of 10. After the sample had been cycled to 400°C for 16 h and slowly cooled to room temperature four times, there was no trace of the (200) fcc line. The sample was then removed from the Ta envelope and placed in the cryostat for a study of the magnetic order.

At 2.5°K the $La_{90}Tb_{10}$ sample shows a broad but well-defined peak approximately 7° from the forward direction, in agreement with results reported by Koehler *et al.*[24] As shown in Fig. 7, the total scattering at 2.5°K (solid dots) exceeds the 78°K scattering over the interval from 5° to 10°. In terms of Bragg plane spacing this corresponds to an interval from 6.6 to 13.2 Å. The statistical errors for these data are about the size of the dots. Although the maximum height is substantially less than the prominent nuclear peaks, the total area is nearly $\frac{1}{2}$ the total area under the (102) peak, the most intense of the nuclear lines. In view of the fact that the Tb-magnetic-scattering cross section is about 4 times the La-nuclear-scattering cross section, it would seem that a large fraction of the Tb ions are scattering into this peak. Unfortunately, preferred orientation may change intensities by as much as 10%, so no definitive statement can be made concerning the fraction of Tb ions contributing to this peak.

As the temperature of the sample increases, the width and general shape of the peak remains unchanged, but the amplitude slowly diminishes as shown in Fig. 8. The error bars here represent the expected statistical fluctuation. A La–20 at.% Tb sample shows qualitatively the same features as the 10 at.% sample. The width is the same but the intensity is correspondingly larger. It is a little surprising that the peak does not broaden as the concentration decreases. This would

[24] W. C. Koehler, J. Appl. Phys. (to be published).

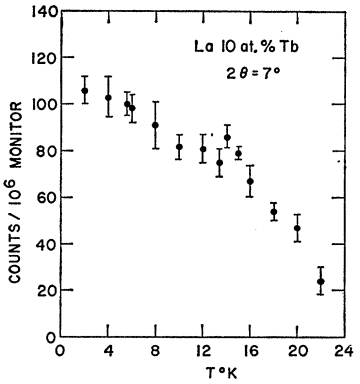

FIG. 8. Temperature dependence of the magnetic peak for La 10 at.% Tb.

seem to indicate that the range of order does not change very much as the concentration decreases from 20 at.% Tb to 10 at.% Tb.

SINGLE-CRYSTAL SUSCEPTIBILITY

In order to understand details of the magnetic structure of these systems it is necessary to perform measurements on single crystals. Unfortunately all of our attempts to grow single-crystal La and dilute La-Tb alloys were failures. The addition of Lu, however, stabilizes the double-hcp structure, and we were able to grow two single crystals of $La_{0.80}$ $Lu_{0.18}$ $Tb_{0.02}$ and two single crystals of $La_{0.80}$ $Lu_{0.15}$ $Tb_{0.05}$. The samples were arc melted into the shape of a finger about 1 in. long and $\frac{3}{8}$ in. diam. This button was then sealed in Ta and annealed for 2 months during which time one large crystal developed. Approximately 20 attempts were made by this method, but only four crystals grew to an appreciable size. After the polycrystalline sections were cut away, the single crystal measured approximately 20×8×4 mm. A piece of this sample was cut for susceptibility measurements.

The apparatus for the differential susceptibility measurements consisted of a standard-heat leak chamber and a 33-Hz ratio transformer bridge with a measuring field of about 1 Oe. Absolute values were assigned by measuring a superconducting $La_{0.80}$ $Lu_{0.20}$ sample with the same geometry, where the susceptibility of the superconductor was assumed to be $-1/4\pi$. Because the sample was a slightly irregular parallelepiped, demagnetizing effects were difficult to estimate, and the absolute values of χ may be in error by 10%. The relative shapes of the curves, however, are much more accurate.

At high temperatures the Tb alloys all follow a Curie-Weiss law with negative Curie temperatures. As shown on Fig. 9, the a-axis and b-axis susceptibilities show a well-defined maximum at 5.7°K and drop to a value far below the Curie Law. Within the accuracy of the measurement, the a-axis and b-axis susceptibilities are identical but the c-axis susceptibility is much smaller. This suggests that there may be a strong anisotropy field holding the moments in the basal plane. If an external field of about 5000 Oe is applied to the sample, the b-axis susceptibility is suppressed to the point that it practically overlays the c-axis zero-field susceptibility. In this respect the Tb alloys are quantitatively quite different from the Gd alloys. Whereas 200 Oe will depress the La-Gd χ maximum by a factor of 2, it takes several thousand Oe to bring a corresponding change in La-Lu-Tb alloys. Measurements on polycrystalline material indicate that the susceptibility of polycrystalline La-Tb alloys[25] is practically the same as the a-axis susceptibility of the $La_{0.80}$ $Lu_{0.15}$ $Tb_{0.05}$ single crystal.

SINGLE-CRYSTAL NEUTRON DIFFRACTION

A neutron-diffraction study was then initiated for the $La_{0.80}$ $Lu_{0.15}$ $Tb_{0.05}$ single crystal to look for any remnant of long-range order. A scan of the nuclear peaks for this sample at 2.5°K shows a double-hcp structure with lattice constants of $a=3.708$ Å and $c=12.00$ Å. Because Nd has the same crystal structure as this alloy with almost the same lattice constants, the initial scans were designed to look for the Nd magnetic structure. When no satellites were found to an accuracy of 0.04% of the 004 peak, saturation radial scans were begun at intervals of 1° in 2θ and at intervals of 1° in the sample table setting over the regions of the a^*-c^* and a^*-b^* planes in reciprocal space that are shaded in Fig. 10. The limiting factor in the resolution of peaks was the presence of a halo [with a magnitude of 0.04% of the (004) nuclear peak] that arose from the aluminum parts of the cryostat. A few peaks were

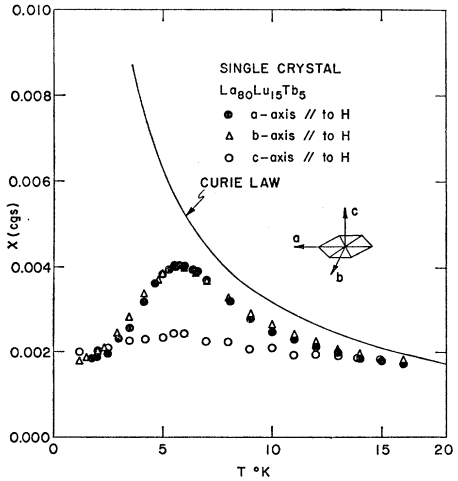

FIG. 9. Single-crystal susceptibility for $La_{0.80}$, $Lu_{0.15}$, $Tb_{0.05}$.

[25] T. S. Prevender, M. S. thesis, Iowa State University (unpublished).

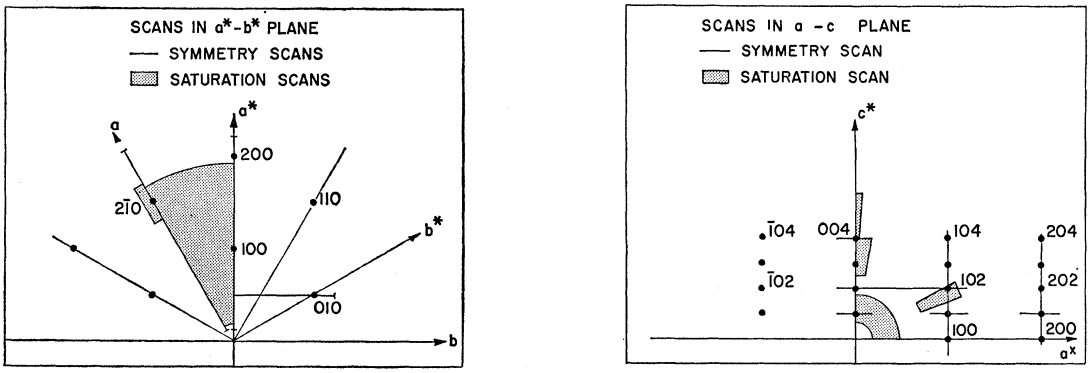

FIG. 10. Neutron-diffraction scans. Solid lines are symmetry scans and the shaded areas are radial-saturation scans.

found with a magnitude of approximately 0.1% of the (004) nuclear peak but these were independent of temperature and randomly situated, so we assume they reflect some impurity. Another irregularity in the results is that the (001), (002), and (003) peaks were not strictly forbidden as expected for the double-hcp structure. When the whole sample was measured on the first run, these peaks had an intensity of 2.5% of the (004) peak, but on a later run, after half of the sample had been cut away for susceptibility measurements, the intensity decreased to 0.2% of the (004) peak. Whatever the origin of these peaks, it was clear that it was not a uniform property of the sample. They could arise from stacking faults along the c axis where one end of the sample was more heavily faulted than the other, but other factors could also contribute. In any case the intensity of all of these reflections is independent of temperature, and the peaks do not seem to be related to the magnetic order.

Several years ago Anderson and Suhl[26] proposed that these dilute alloys might exhibit cryptoferromagnetism, a ferromagnetic structure with very small domains that point in random directions. If the Tb ions were to order ferromagnetically, the intensity of the nuclear peak should increase by about 1%, so these reflections were carefully studied. Intensity measurements at 78 and at 2.5°K show no change in the (100) peak to an accuracy of 0.04% and no change in the (210) to an accuracy of 0.1%. For the (004) peak, we only measured the counting rate at 3 points near the top of the peak, but we can say that the peak height does not change by more than 0.3%. This rules out any ferromagnetic or cryptoferromagnetic structure.

At this point it was decided to investigate the paramagnetic scattering in somewhat more detail. From other experiments with paramagnetic scattering in a Tb–50 at.% Ho sample the beam intensity, counter efficiency, and other factors were estimated, and the paramagnetic counting rate for our sample was calculated to be 1.7 counts/min at 7° from the forward direction. With the sample oriented at 5° from the a^* axis in the a^*-b^* plane and 2θ set at 7°, the counting rate was measured at 78 and at 2.5°K to be the same to an accuracy of 0.1 count/min. Hence the paramagnetic scattering changes by less than 10% when the material orders.

[26] P. W. Anderson and H. Suhl, Phys. Rev. **116**, 898 (1959).

CONCLUSIONS

On the basis of the neutron-diffraction and susceptibility results for the $La_{0.80}$ $Lu_{0.15}$ $Tb_{0.50}$ single crystal, it would appear that there is an anisotropy field that pulls the moments into the basal plane, but in the basal plane there is no long-range order of the spins. The short-range order peak in the forward direction, which had been presented for the $La_{0.80}$ $Tb_{0.20}$ and $La_{0.90}$ $Tb_{0.10}$ samples, is at least 200 times less intense for the 5 at.% Tb sample, and the paramagnetic scattering does not change as the temperature is lowered through the susceptibility maximum to a temperature less than $\frac{1}{2}T_M$. Below the susceptibility maximum, the neutron scattering appears to be an independent ion effect, and there is no evidence for additional scattering which would arise from the formation of a polarization of conduction electrons around the impurity site. If the ion were spin-compensated by the conduction electrons, as suggested by many theories,[27] there would be a change in the paramagnetic scattering. None is observed to an accuracy of 10%. The magnetic ions appear to line up with respect to some sort of local field to give a state with the full Tb moment randomly oriented in the basal plane.

ACKNOWLEDGMENTS

We would like to thank J. Moorman and B. J. Beaudry for their assistance in preparing the samples for this work and it is a pleasure to acknowledge valuable conversation with S. K. Sinha, T. O. Brun, Y. Ito, and S. H. Liu.

[27] K. Yosida, Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966); J. Kondo, *ibid.* **36**, 429 (1966); J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).