of Sec. IVA indicates that acoustical mode scattering is still important. Optical mode scattering is nearly frozen out at this temperature so the energy independent mechanism used for comparison has been labeled μ_N corresponding to scattering by neutral impurities.[27] Such a mechanism is at least a possibility although considerations given in Sec. IVA argue against it.

As the temperature is lowered from 19° to 6°K the mobility increases only slightly. However, as Fig. 9 indicates, the high field effect has become considerably more important. This appears to be due to the importance of impurity scattering at the lower temperature and is just the result expected from the amount of scattering chosen to fit the mobility data as discussed in Sec. IVC. The general shape of the theoretical curve in Fig. 9 is in good agreement with experiment for scattering by charged centers ($p=\frac{3}{2}$) but does not agree well in the case of acoustical scattering ($p=-\frac{1}{2}$).

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Properties of Some Magnetic Superconductors

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Two solid solutions in the system $GdRu_2-CeRu_2$, in which both ferromagnetism and superconductivity have been observed, are studied by magnetic methods. The solid solution $Gd_{0.082}\,Ce_{0.918}\,Ru_2$, which has a Curie point θ above the critical temperature T_s for superconductivity, is both ferromagnetic and superconducting. In $Gd_{0.04}\,Ce_{0.96}\,Ru_2$, for which the expected $\theta<T_s$, no ferromagnetic moment could be measured, although a small moment may be present and not detected by our methods. In solid solutions of increasing Gd content, when θ begins to exceed the expected T_s by a considerable margin, T_s suddenly drops toward zero; and when $T_s>\theta$, θ approaches zero. Similar conclusions apply to the system $GdOs_2-LaOs_2$ when θ and T_s are related in the same ways. Both major and minor hysteresis loops have forms not previously observed and enable one to detect ferromagnetism and superconductivity when they exist. The molecular fields resulting from the interaction between Gd atoms, and the Curie points calculated therefrom by molecular field theory, increase with increasing temperature; this is in accordance with the theory of long-range exchange forces developed by Brout.

SUPERCONDUCTIVITY and ferromagnetism have been studied in a number of metallic compound systems by Matthias, Suhl, and Corenzwit.[1] The present paper reports more detailed studies of solid solutions in the system $CeRu_2$-$GdRu_2$ and of some other materials. The purpose of the work[2] has been to find out if superconducting materials can become ferromagnetic and if ferromagnetic materials can be superconducting at the same time, and more generally to know the influence of the one property on the other.

EXPERIMENTAL METHOD

Measurements have been made of magnetic moment as dependent on field strength H, and temperature T, over the range $H=0$ to 12 000 oe, $T=1.3$ to 300°K. Moments were usually measured by a null method using a pendulum magnetometer supporting the specimen in a field gradient, with strain gauge sensing elements, as previously described.[3] On some occasions the material was surrounded by a search coil, the field reversed (or the the sample and coil rotated 180°) and a galvanometer deflection noted. Hysteresis loops were measured using the pendulum magnetometer in a carefully calibrated electromagnet, taking into account the nonlinearity and hysteresis of the magnet and in some cases the field produced at the specimen by the current through the balancing coil, which annuls the moment of the specimen. The initial magnetization curves were measured after cooling from a sufficiently high temperature in zero field.

The materials were prepared by melting in the argon arc. X-ray examination showed them to be true solid solutions with, in some cases, a trace of uncombined ruthenium.

The specimens, having usually a dimensional ratio of about 4, were mounted at the center of the balancing coil. The sensitivity of the pendulum magnetometer was about 0.004 cgs unit in high fields, the largest moment measureable being about 40. Since the gradient was approximately proportional to the field strength, the sensitivity decreased with the decreasing field to zero at $H=0$ and measurements were not usually made with this method when $H<50$ oe; in measuring hysteresis loops the moment in zero field could be obtained by interpolating between the points for $H=\pm 50$.

[1] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 449 (1958).
[2] For a brief report of part of this work see J. Appl. Phys. **31**, 235 (1960).
[3] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956); R. M. Bozorth and D. D. Davis, Phys. Rev. **118**, 1543 (1960).

CURIE POINTS AND SUPERCONDUCTING TRANSITIONS

Materials of the composition $Gd_{0.04}\,Ce_{0.96}\,Ru_2$ and $Gd_{0.082}\,Ce_{0.918}\,Ru_2$ were first examined, for previous experiments had indicated that the first of these compositions became superconducting on cooling before it was expected to be ferromagnetic (as judged from the extrapolation of the θ vs composition curve to $\theta=0$ at zero concentration of gadolinium); the second became ferromagnetic before it became superconducting. Data used for determination of θ are shown for the second material in Fig. 1, where σ_m is the magnetization per mole of MRu_2. Three methods were used to derive θ from the data: (1) the classical Weiss-Forrer method, whereby H is plotted vs T at constant $\sigma_m=\sigma_0$ and extrapolated to $H=0$ to give T_0, and then the line σ_0^2 vs T_0 extrapolated to $\sigma_0^2=0$ to give $T_0=\theta$; (2) reversal of specimen and surrounding search coil in fields of 5 to 50 oe, to give a galvanometer deflection that is proportional to the initial susceptibility, which is normally a maximum at $T=\theta$; and (3) determination of the molecular field constant from the magnetization curve by a method to be described in a later section. All three of these methods gave $\theta=6.3°\pm0.2°$K for the 8.2% material.

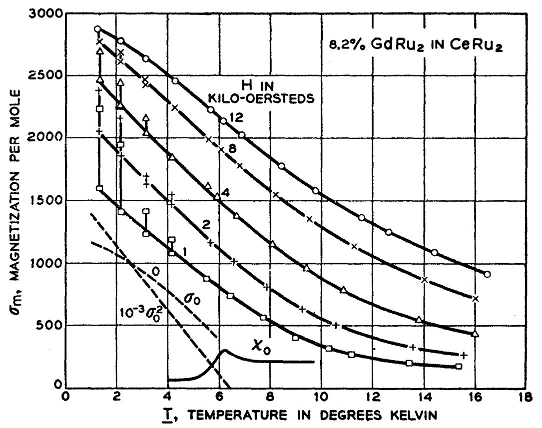

FIG. 1. Magnetization of $Gd_{0.082}\,Ce_{0.918}\,Ru_2$ vs temperature for various field strengths, showing method for determining Curie point, 6.3°K, by double extrapolation. χ_0 curve also shows Curie point. Double values show hysteresis.

The σ_m vs T curves of Fig. 1 show double values of σ_m when $T<5°$K; these points were measured when the values of field strength applied immediately before measurement in field H were, respectively, +12 and −12 koe, the differences between the values of σ_m being due to hysteresis resulting from either ferromagnetism or superconductivity.

Determination of the temperature T_s at which superconductivity disappears was made by cooling the specimen in zero field to a given temperature and then measuring the initial magnetization curve, as shown in Fig. 2. The material is superconducting as long as $d\sigma/dH<0$,

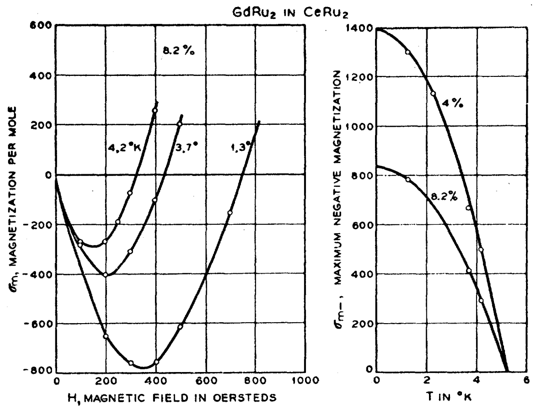

FIG. 2. Initial magnetization curves for the 8.2% material, and treatment for determining critical temperature for superconductivity. Curves at right are true parabolas.

since in a superconducting material $B=H+4\pi I=$ constant and $dI/dH=(\rho/M)\times d\sigma_m/dH=-1/(4\pi)$, where ρ is the density and M the molecular weight. To determine T_s the (negative) value of σ_m at the minimum of the curve is plotted vs T, as shown in Fig. 2(b), and a parabola passed through the various points and extrapolated to the axis of temperature.

The values of T_s and θ so determined are plotted in Fig. 3, together with points measured by Matthias *et al.*[1] for 0, 2, and 13% $GdRu_2$ using somewhat different methods. The 10% alloy gave no sign of superconductivity at 1°K.

Although the detection of superconductivity in the presence of ferromagnetism is easy, for in this case the initial susceptibility χ_0 is negative, the presence of ferromangerism in a superconductor is difficult. In this paper we establish a criterion in terms of the hysteresis, as now to be discussed.

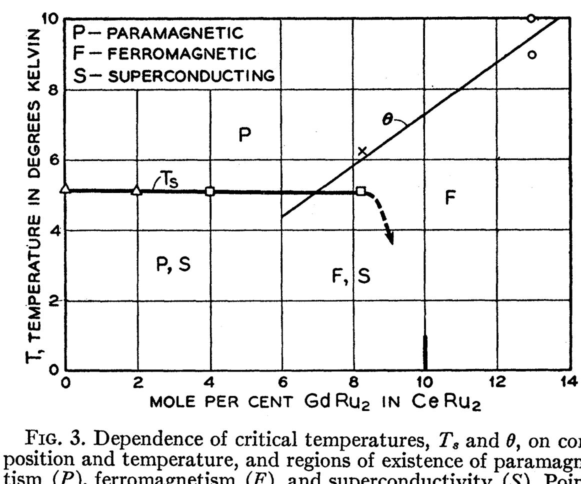

FIG. 3. Dependence of critical temperatures, T_s and θ, on composition and temperature, and regions of existence of paramagnetism (*P*), ferromagnetism (*F*), and superconductivity (*S*). Points ○ and △ from reference 1; points □ and × from our data, confirmed by Matthias. The boundary between *P,S* and *F,S* is uncertain.

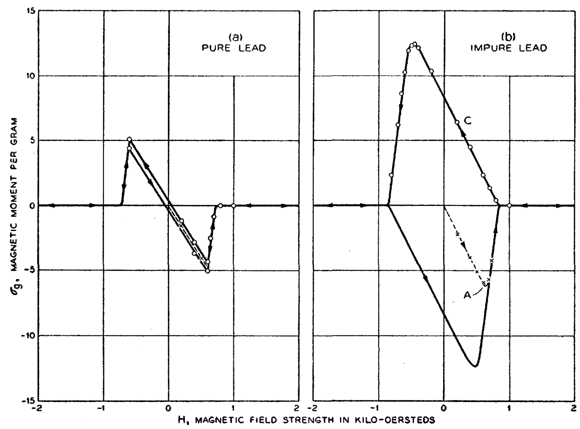

FIG. 4. Magnetic moments of (a) pure annealed and (b) impure strained lead, showing frozen-in moment in (b).

HYSTERESIS LOOPS

It is well known[4] that the initial susceptibility curve and the hysteresis loop of a nonmagnetic superconductor depend on the purity of and stress in the material. To illustrate this point, the data of Fig. 4 were taken with specimens of (a) 99.99% pure annealed lead and (b) a hammered lead solder containing 1.7% Ag and 1.0% Sn, each with a dimensional ratio of about 2. After the initial (negative) magnetization, application of a high field, and its subsequent reduction, the flux in the impure lead, in contrast to the pure, is "frozen in," and the ordinate of the midpoint of the upper straight side of the loop, at C, is about equal to the maximum negative ordinate of the initial curve, A. If magnetic hysteresis were superposed on the superconductivity, the whole upper half of the loop would be raised and the equality of the ordinates would no longer exist.

In Fig. 5 the hysteresis loop of the material containing 4% of $GdRu_2$ in $CeRu_2$, taken at 4.2°K, shows

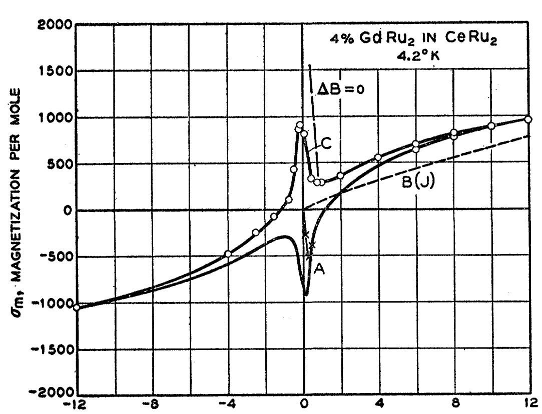

FIG. 5. Hysteresis loop, slope for constant flux (superconduction), and Brillouin curve for 4% material at 4.2°K.

[4] D. Shoenberg, *Superconductivity* (University Press, Cambridge, England, 1952).

paramagnetism and superconductivity, the former by the approximate equality of the ordinates at A and C and by the height of the loop at 12 koe, the latter by the negative slope $d\sigma_m/dH$ in fields low enough to permit the superconduction to reappear after having been suppressed by the more intense fields. The broken curve $B(J)$ is the Brillouin function (for zero molecular field) plotted for the known gadolinium content using $J=\frac{7}{2}$, $g=2$. The fact that it lies somewhat below the observed curve in high fields indicates some molecular field, but not enough to make it ferromagnetic at this temperature.

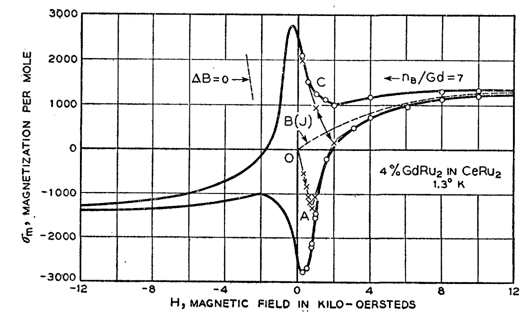

FIG. 6. Loop for 4% material at 1.3°K.

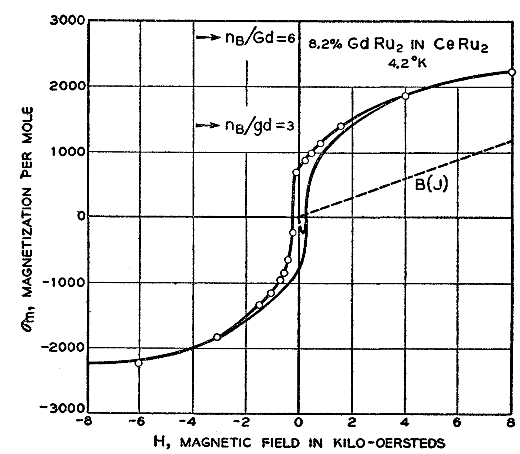

FIG. 7. Loop for 8.2% alloy at 4.2°. Loop is normal in form, initial curve shows slight superconductivity.

At the lower temperature of 1.3°K, the loop of Fig. 6 shows superconductivity with a higher critical field strength, as expected, and also a magnetization much nearer to the Brillouin curve, as compared with the curve for 4.2°. This implies that the molecular field at 1.3° is even less than at 4.2°, and the tendency previously shown toward ferromagnetism is now decreased and is apparently nonexistent. However, the data cannot rule out the presence of a small ferromagnetic moment.

Data for the 8.2% material show quite a different behavior. The loop for 4.2° (Fig. 7) appears to be that of a normal ferromagnetic material except for the small

initial negative susceptibility. The position of the $B(J)$ curve, as well as the maximum in the initial susceptibility curve (χ_0 in Fig. 1) substantiate its ferromagnetism. The loop for 1.3° (Fig. 8) also shows that the material is at the same time ferromagnetic and superconducting at this temperature; ferromagnetic remanence is shown by the great difference between the ordinates for the points A on the initial curve and C at the middle of the superconducting portion of the loop. The material may be a composite of superconducting and ferromagnetic domains, possibly the very small domains proposed by Anderson and Suhl[5] and called by them "cryptoferromagnetism."

Hysteresis loops were also measured for two solid solutions in the system[6] $GdOs_2$-$LaOs_2$. We now designate by θ' the Curie point to be expected if the θ vs composition curve is a straight line passing through the origin and the measured Curie points for high concentrations of $GdOs_2$. In the two materials of this system that we examined, $Gd_{0.045}$ $La_{0.955}$ Os_2 and $Gd_{0.09}$ $La_{0.91}$ Os_2, we have, respectively, $T_s > \theta'$ and $\theta = \theta' > T_s$. The loops for 1.3°, in Figs. 9 and 10, are similar in kind to

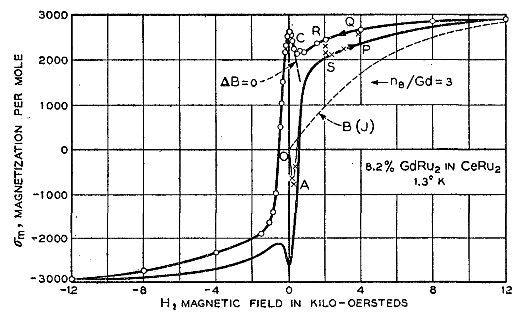

FIG. 8. Loop for 8.2% alloy at 1.3°, showing ferromagnetism and superconductivity.

those for the $GdRu_2$-$CeRu_2$ system in that the positions of the $B(J)$ curves and the ordinates for the positions A and C both indicate absence of ferromagnetism in the first alloy and its presence in the second, and both loops show the negative $d\sigma_m/dH$ characteristic of superconductivity.

In view of the results already described, the diagram of Fig. 3 has been labeled to show the regions in which the ferromagnetic (F), paramagnetic (P), and superconducting (S) phases are present. The position of the boundary between the regions P,S and F,S is uncertain and so has been omitted.

MINOR LOOPS

In the major loop for $Gd_{0.04}$ $Ce_{0.96}$ Ru_2 it was noticed that the ascending and descending branches were substantially separated at moderate and high fields even though there was no evidence of ferromagnetism. Minor

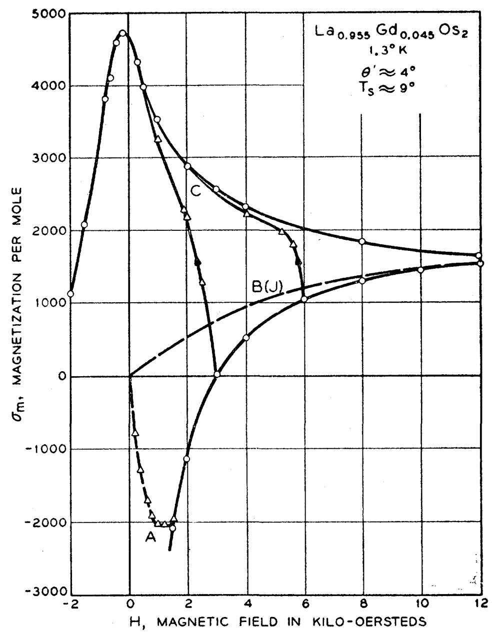

FIG. 9. Initial magnetization curve and loop for $Gd_{0.045}$ $La_{0.955}$ Os_2 showing superconductivity and paramagnetism.

loops in this range were measured (Fig. 11) and the slopes of the sides of the loop, taken when an increasing field was changed to a decreasing one, and when a decreasing field was changed to an increasing one, were found to correspond to superconduction: $\Delta B = 0$ or $dI/dH = -1/(4\pi)$. Thus all of the separation between the ascending and descending parts of the major loop can be accounted for by superconduction alone.

Upon cooling of the $Gd_{0.04}$ $Ce_{0.96}$ Ru_2, the presence of ferromagnetism, if it exists, or even a tendency toward ferromagnetic behavior, might make itself known in some kind of discontunity in the magnetic properties at $\theta' = 3°$. Accordingly, the vertical distance between the two branches of the loop at $H = 3$ koe were measured for various temperatures and are plotted in the insert of

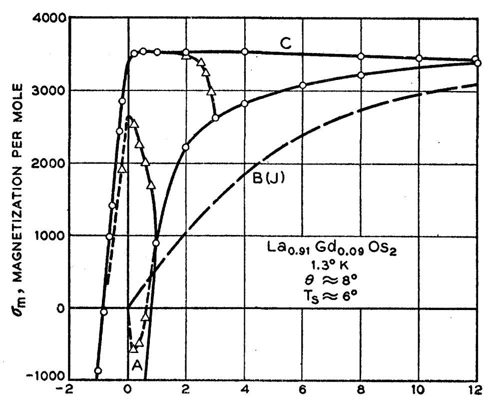

FIG. 10. Loops for $Gd_{0.09}$ $La_{0.91}$ Os_2 showing superconductivity and ferromagnetism.

[5] P. W. Anderson and H. Suhl, Phys. Rev. **116**, 898 (1959).
[6] V. B. Compton and B. T. Matthias, Acta Cryst. **12**, 651 (1959).

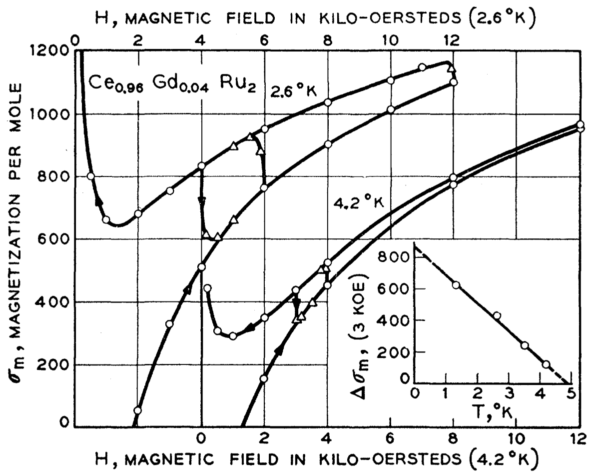

FIG. 11. Minor loops for $Ce_{0.96}$ $Gd_{0.04}$ Ru_2 at two temperatures, showing superconductivity in high fields, and variation of loop height (at 3 koe) with temperature.

Fig. 11. The line connecting the points was found to be straight within the experimental error, and it extrapolated nearly to the already known temperature T_s; no irregularity is observed.

A portion of a minor loop is also shown in Fig. 9 for $Gd_{0.045}$ $La_{0.955}$ Os_2.

It has been proposed[7] that the hysteresis in the minor loops may be associated with the fields around the Bloch walls in ferromagnetic domains. In our experiments, however, these loops have been observed when the material is not even suspected of being ferromagnetic, as in the 4% material at 3.5 and 4.2°K (when $T_s > T > \theta'$), and so can contain no Bloch walls.

It is not surprising to find evidence of superconductivity in fields so much above that at which the superconduction of the material as a whole is destroyed. The existence of regions of abnormally high critical field has been postulated to explain the absence of a Meissner effect in alloys.[8] In Mendelssohn's proposed "sponge" structure, the meshes of the sponge are presumed to have a much higher critical field than the enclosed material, and domain studies show the intricate patterns[9] assumed when the magnetic field is increased in strength. Also, careful measurements of resistivity as dependent on field strength show that in many cases the normal resistance of an alloy is restored by application of a magnetic field only when the field strength is many times that necessary to restore the first trace of resistance.

It is concluded that the minor loops are a phenomenon of superconductivity and are not connected with ferromagnetism.

Note added in proof.—Minor loops with steep sides have been observed in superconducting YOs_2. Since no magnetic moment was measurable at 12 koe, the minor loops cannot be due to ferromagnetism but only to superconductivity.

SUSPENSION OF IRON IN MERCURY

It is interesting to compare the magnetic properties of the materials described above with those of a suspension of a ferromagnetic material in a superconductor, the superconductor being nonferromagnetic and the ferromagnetic material nonsuperconducting. Such a suspension, of about 1% iron in mercury, was kindly provided us by Dr. Paine and Dr. Luborsky of the General Electric Company.

Measurements of the initial magnetization curve and the hysteresis loop are recorded in Fig. 12. The material behaves in some respects like the alloys described above: the initial negative susceptibility, the negative slope $d\sigma/dH$ on the major hysteresis loop, and the substantial magnetization in high fields, are characteristic of the suspension and of some of the alloys. The midpoint C of the straight portion of the loop exceeds the greatest negative excursion of the initial curve, A, by about 0.7 unit in σ_g (moment per gram), and this is about the magnetic remanence obtained by extrapolating the upper half of the hysteresis loop back to $H=0$; this shows that the frozen-in moment is superposed on the ferromagnetism. The minor loop increasing from $H=400$ shows no superconductivity but purely ferromagnetic behavior, in contrast to that of the compounds reported. This is to be expected since the critical field of bulk mercury at this temperature is somewhat less than 400 oe, and is not in this case increased by subdivision or severe strain. The vertical height of the loop in fields higher than 400 oe is then to be ascribed entirely to ferromagnetic hysteresis.

The difference in the behavior of the suspension and of the 8.2% material indicates that in the latter case we have a more intimate connection between the superconductivity and ferromagnetism.

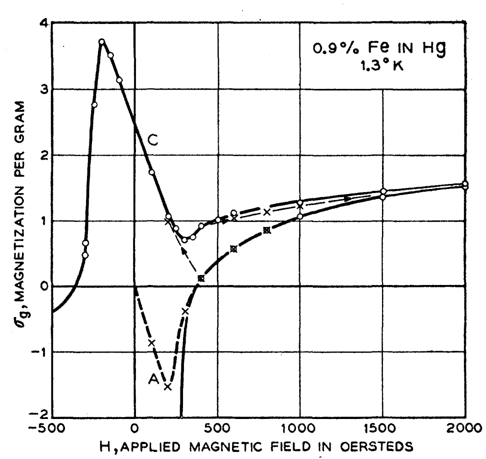

FIG. 12. Magnetization curve and hysteresis loop for colloidal suspension of ferromagnetic iron in superconducting mercury.

[7] B. T. Matthias and H. Suhl, Phys. Rev. Letters 4, 51 (1960).
[8] See reference 4, pp. 41, 44.
[9] A. L. Schawlow and G. E. Devlin, Phys. Rev. 110, 1011 (1958), and earlier reference therein.

ERBIUM-LANTHANUM ALLOY

A hysteresis loop of a solid solution[10] of 4.9% Er in La, at 2.2°K, showed the peculiar behavior illustrated in Fig. 13(a) with two maxima close together. In order to be sure of the reality of the effect three sets of measurements were carefully made. The loss in moment at about $H=-200$ oe was precipitous. The explanation is apparent when the ordinates are converted to $B=H+4\pi\sigma_m\rho/M$ as in Fig. 13(b): the flux is suddenly and completely expelled, then an additional negative field at first causes no change in flux, but change does take place when the field begins to reduce the superconduction.

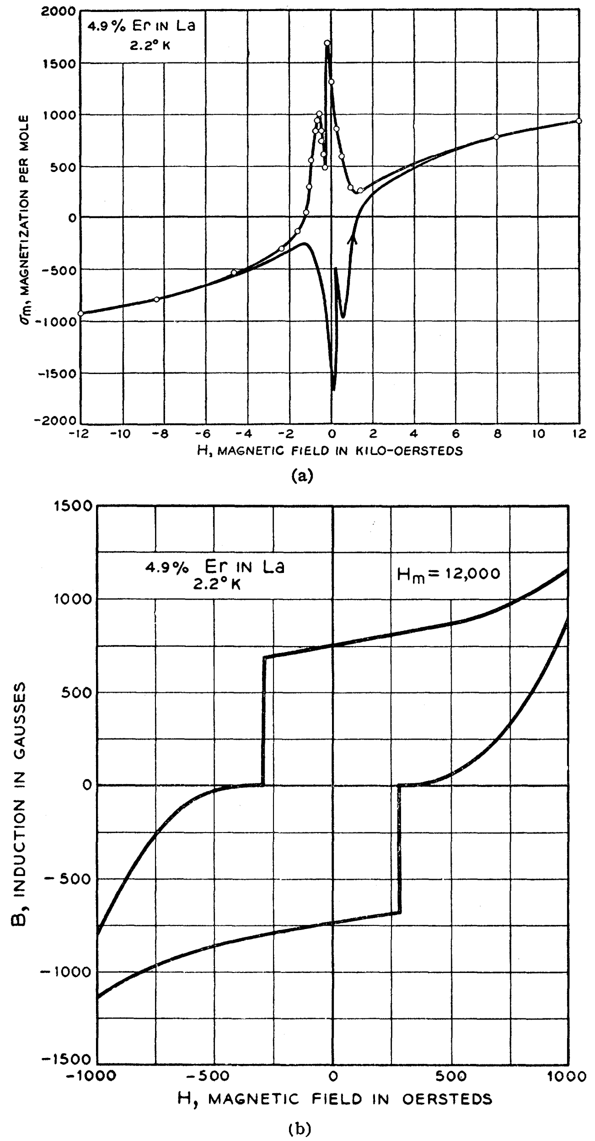

FIG. 13. (a) Hysteresis loop of 4.9% Er in La metal showing double peak when σ_m is plotted vs H; (b) loop when B is plotted vs H.

[10] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 92 (1958).

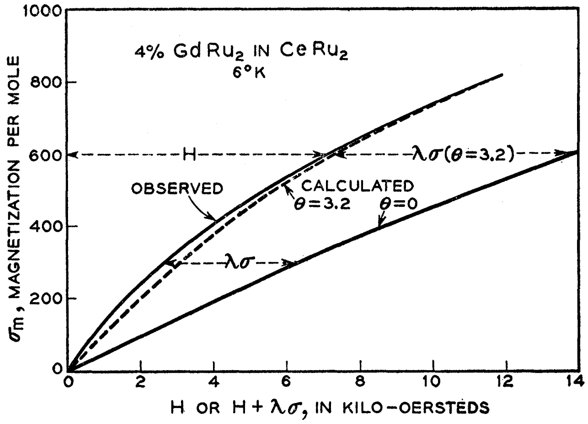

FIG. 14. Illustration of effect of molecular field, $\lambda\sigma$, on magnetization curve.

CURIE POINTS AND MOLECULAR FIELD

In theory it is possible to determine the Curie point from the magnetization curve measured at a temperature some distance above the Curie point. We start with the Brillouin function:

$$\frac{\sigma}{\sigma_0}=\frac{2J+1}{2J}\text{ctnh}\frac{(2J+1)a}{2J}-\frac{1}{2J}\text{ctnh}\frac{a}{2J},$$

and take account of the molecular field, $\lambda\sigma$, by using

$$a=Jg\beta(H+\lambda\sigma)/kT.$$

Since spontaneous magnetization disappears[11] at

$$\theta=(J+1)g\beta\lambda\sigma_0/3k,$$

we find by combining the above relations that

$$\theta=\frac{(J+1)g\beta}{3k(\sigma/\sigma_0)}\left(\frac{akT}{Jg\beta}-H\right).$$

If we now select a given value of a, calculate the corresponding σ/σ_0, and note the experimental value of H for this σ/σ_0, θ is readily derived. The symbols have their usual significance, and for atoms with a Gd^{3+} core we have $J=\frac{7}{2}$, $g=2$, $\sigma_0=NJg\beta$, so that

$$\theta=0.202(2.13aT-H_k)/(\sigma/\sigma_0),$$

H_k now being the observed field strength in kilo-oersteds.

The above derivation is probably most applicable to Gd among all the magnetic atoms since there is here no spin-orbit coupling and the $4f$ shell responsible for the magnetic moment is surrounded by a filled $5s$ shell. Gd in both ionic and metallic form is observed to have the theoretical saturation moment determined by J and g.

An example of the method is shown in Fig. 14. The upper curve is observed, the lower one is calculated for

[11] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 431.

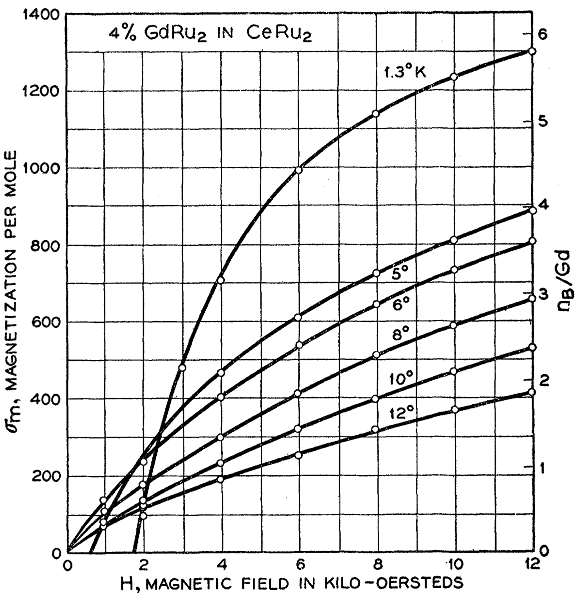

FIG. 15. Magnetization curves of the 4% $GdRu_2$ material, used for evaluation of molecular field and Curie point. Below 6° curves show hysteresis due to superconductivity.

a molecular field coefficient $\lambda=0$. The horizontal difference between the curves, as shown at $\sigma_m=600$, is the contribution of the molecular field. The derived value of θ is then (0.202/0.43) (14.0–7.2) = 3.2°K. The various values of θ so determined should be constant for all values of σ/σ_0 at any given temperature, but may very well change with temperature because the exchange interaction may vary, as one might expect in considering the mechanism of exchange through conduction electrons. The magnetization curve calculated from the Brillouin function for $\theta=3.2°$ is shown by the broken line in the figure; the lack of perfect agreement may well be due to the small moment attributable to cerium.

The data used for calculating θ for $Gd_{0.04}Ce_{0.96}Ru_2$ are given in Fig. 15. Measurements of magnetic moment were made in increasing fields after a high negative field had been applied. The existence of hysteresis (due to superconductivity) is shown in the curves for 1.3 and 5°K that have a zero moment when $H>0$.

The θ's derived from the data are plotted for the two materials in Fig. 16. The true Curie point is of course at the intersection of the curve for the calculated θ with the line for $T=\theta$, and this intersection for the 8.2%, material agrees well with the θ determined directly by other means, 6.2°K. This agreement shows the adequacy of the molecular field treatment for determining the Curie point. The 4% specimen becomes superconducting before the intersection, as may be seen in Fig. 15, but extrapolation of the line of Fig. 16 is toward $\theta=2.5°$, nearly the expected Curie point θ' obtained by extrapolating the θ vs composition line to the origin. We conclude that above the critical temperature T_s the material behaves as if it would become ferromagnetic at about 2.5°, but intervention of superconduction depresses θ toward zero as indicated by the form of the hysteresis loop at 1.3° (Fig. 6).

It was intended at first to apply the molecular field theory to superconducting materials in fields high enough to destroy the superconductivity, but it was found that traces of superconduction usually remained in the highest fields available, as shown above by the character of the minor hysteresis loops. The method would be applicable to superconducting materials in which all traces of superconductivity are removed by the application of sufficiently weak fields. Experiments on a material with such a low critical field are to be described in a forthcoming article.[12]

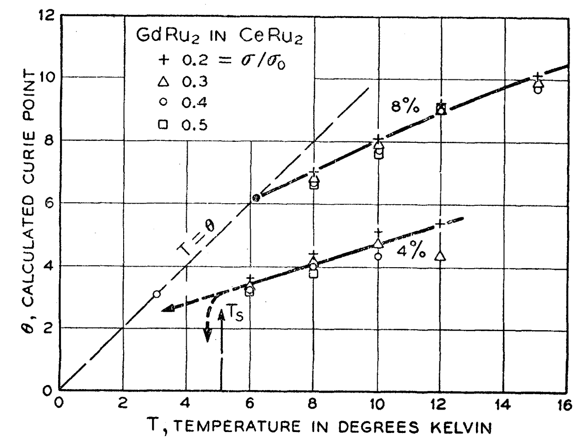

FIG. 16. Calculated Curie points, θ, of two solid solutions showing variation of θ with temperature. True Curie point agrees with calculated θ for 8.2% material but is depressed at or near T_s for 4% material.

The change of the derived θ with T is in accordance with the theory of Brout[13] for dilute alloys in which there are long-range exchanges forces. Changes of the molecular field constant of iron and nickel with temperature have long been known.[14]

ACKNOWLEDGMENTS

We are indebted to E. Corenzwit for the preparation of the materials, to Mrs. V. B. Compton for the x-ray examination, and to B. T. Matthias, H. Suhl, and P. W. Anderson for discussion of the results. The collodial suspension of Fe in Hg was kindly supplied by T. O. Paine and E. Luborsky of the Research Laboratories of the General Electric Company.

[12] To be presented at the Seventh Conference on Low Temperature Physics, Toronto, August 29, 1960.
[13] R. Brout (private communication).
[14] H. H. Potter, Proc. Roy. Soc. (London) **146**, 362 (1934).