It is interesting, anyway, that Mn, the transition element more favored for the formation of localized magnetic states, produces the strongest depression.

In conclusion, a very sharp demonstration of the effect of magnetic states on superconductivity was given; the measurement of critical transition temperatures can be a very sensitive test to detect the presence of these magnetic states.

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COLES: At Imperial College, Mr. D. Farrell has been examining zinc alloys containing Mn and Fe. We have confirmed that manganese has a magnetic moment, and the superconducting measurements show a very rapid fall in T_c in agreement with Dr. Boato's measurements. While in Zn–Fe there seems to be little or no moment on the Fe atoms, and the fall in the transition temperature is certainly less rapid, the details are complicated by extremely small solubility of Fe in Zn. This behavior is very striking if there is really a difference between iron and manganese for the same solvent.

G. BOATO, *Universita di Genova:* I should like to add that, contrary to the result in Leiden reported by Professor Gorter, we find that Fe in Al depresses T_c a little bit. It is very difficult to dissolve Fe in Al so that it is a more difficult alloy to study.

M. F. MERRIAM, *University of California:* Dr. Seraphim of IBM and myself have recently measured the effect of dissolved Mn on the transition temperature of indium. Although we were unable to dissolve very much Mn, the initial effect is quite clear and is in general agreement with the results which you describe for Mn–Zn. In particular the value for dT_c/dp is about 65 or 70. In practical terms this means a depression of 60 to 70 mdeg for a resistance ratio of 1000.

Ac Susceptibility Measurements on Transition Metal Superconductors Containing Rare Earth and Ferromagnetic Metal Solutes

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INTRODUCTION

We have applied the complex ac susceptibility technique[1,2] to the study of two problems in transition metal alloy systems. These are (1) the question of simultaneous ferromagnetism and superconductivity in the system $Gd_xTh_{1-x}Ru_2$, as reported by Bozorth *et al.*,[3] and (2) the apparent enhancement of superconductivity caused by dissolving small amounts of iron and ruthenium in titanium. It was found by Matthias *et al.*[4] that small amounts of dissolved iron raised the transition temperature of Ti much more than could be explained by valence effects.

METHOD

In some earlier papers,[1,2] we have shown that in zero-field superconducting transitions the presence of a maximum in the imaginary part of the complex susceptibility χ'' indicates filamentary structure. We have explained the maximum by a model in which the average conductivity of the specimen increases in the transition region but in which no Meissner effect appears. The mechanism suggested is the development and growth with temperature of a distribution of originally unconnected superconducting filamentary inclusions which eventually join to form a multiply connected mesh. In these filamentary materials we observe that the ballistic transition always occurs at a lower temperature that the maximum in χ''; the ballistic transition is interpreted as the point at which the filaments begin to connect up.

The real part of the susceptibility χ' is monotonic with T in superconducting transitions. For a long cylinder of normal metal with increasing conductiv-

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1 E. Maxwell and M. Strongin, Phys. Rev. Letters **10**, 212 (1963).

2 M. Strongin and E. Maxwell, Phys. Letters **6**, 49 (1963).

3 R. M. Bozorth, B. T. Matthias, and D. D. Davis, in *Proceedings of the Seventh International Conference on Low Temperature Physics* (University of Toronto Press, 1961), p. 385.

4 B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1959).

ity, the amplitude of the maximum in χ'' is 0.4 $\Delta\chi'$, where $\Delta\chi'$ = the change in χ'. If in a superconducting transition the amplitude of the peak in χ'' is a significant fraction of $\Delta\chi'$, say greater than 10%, and if the ballistic transition does not coincide with the ac transition (in χ'), then it may be assumed that a homogeneous bulk transition is not being observed. If, in addition, multiple peaks in χ'' are observed, it is reasonable to infer that the sample is physically inhomogeneous and that the different peaks correspond to separate transitions occurring in different parts of the specimen. Since each peak is associated with only a fraction of the total volume, its amplitude should be smaller than for the single peak case.

SAMPLE PREPARATION

The samples used in this investigation were prepared in a gettered argon arc and were then measured in the "as-cast" state. The sample shape was generally oblate spheroidal.

SPECTROGRAPHIC ANALYSIS

The $Gd_xTh_{1-x}Ru_2$ samples had less than 50 ppm iron and the ratio of rare earth impurity atoms to Ru atoms was less than 5×10^{-5}.

The Ti crystal bar we used had 75 ppm Mn and less than 10 ppm Fe.

THE SYSTEM $GD_xTH_{1-x}RU_2$

Some data for this system are shown in Fig. 1. We have also made measurements on Bell Laboratory samples which were kindly supplied to us by Dr. B. T. Matthias and Mrs. V. B. Compton. Although our results differ in many details from the Bell Laboratory data, we do find both ferromagnetism and superconductivity in the same sample. Before discussing the details of the transitions we point out the following differences:

1. The lattice parameters of the Bell Laboratory samples are significantly larger than those of our samples of the same nominal composition—indicating the possibility that the Bell Laboratory samples have less $GdRu_2$ in solution.

2. The superconducting transition temperatures of the Bell Laboratory samples, as measured by Bozorth *et al.*, are significantly lower than the transition temperatures we measured for the same samples.

3. In general our measurements on the Bell Laboratory samples yield somewhat lower transition temperatures than measurements on our samples of the same nominal composition. This suggests that we are getting less $GdRu_2$ in solution which contradicts the lattice parameter data. This discrepancy implies that the compounds obtained by arc melting might be more complicated than originally supposed.

In Fig. 1 we show the transition temperatures for a set of samples that x-ray and preliminary metallographic examination indicate are uniform. Since we have not examined different parts of the specimens and have tried only one etching solution, we do not feel that we can eliminate the possibility of a small amount of some other phase. The fact that multiple peaks are observed in χ'' does appear to indicate that there are at least some inhomogeneities in the samples. Furthermore, because the behavior of χ'' is characteristic of filamentary transitions we cannot

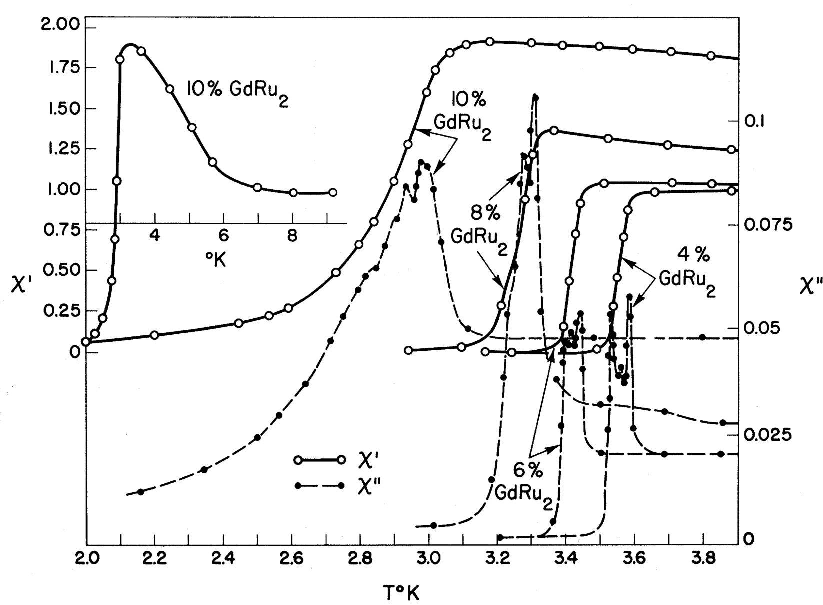

FIG. 1. Zero-field transitions in $Gd_xTh_{1-x}Ru_2$ system. Frequency of ac field of 0.04 Oe was 18 cps. Both χ' and χ'' are in the same arbitrary units, $\chi' = 0$ "superconducting," $\chi' < 1$ diamagnetic, $\chi' > 1$ paramagnetic. Some data points are omitted for clarity.

say that these samples are simultaneously superconducting and ferromagnetic on a microscopic scale. It is interesting to note that we have observed behavior substantially identical to the behavior of the transitions shown in Fig. 1, with samples of the same

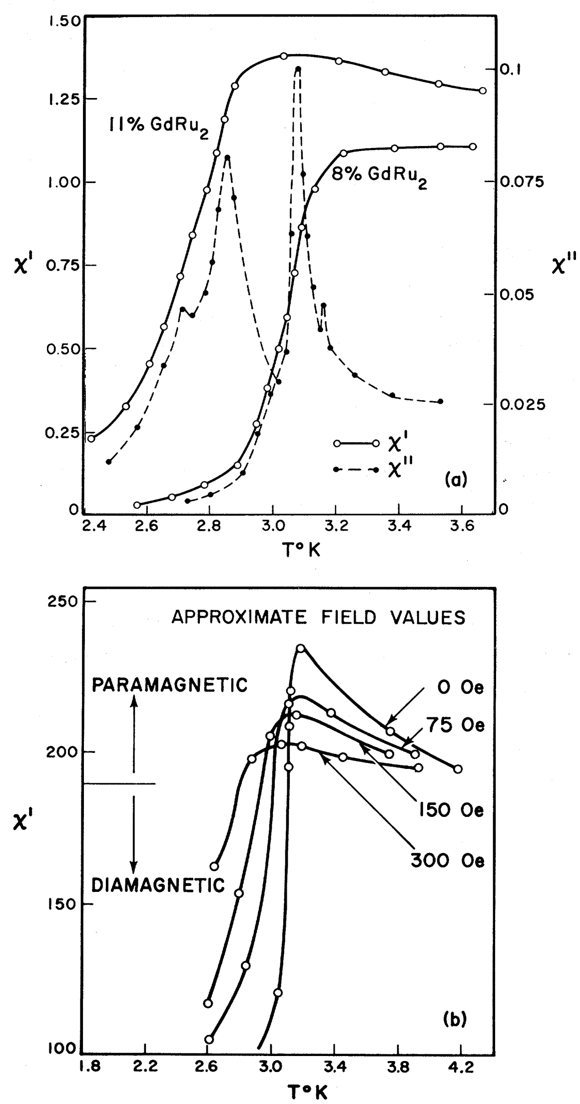

FIG. 2(a). Zero-field transitions in two phase $Gd_xTh_{1-x}Ru_2$ system. Frequency of ac field of 0.04 Oe was 18 cps. Both χ' and χ'' are in the same arbitrary units, $\chi' = 0$ "superconducting," $\chi' < 1$ diamagnetic, $\chi' > 1$ paramagnetic. Some data points are omitted for clarity. (b). dc field behavior of 8.6% $GdRu_2$ alloy. Frequency of ac field of 0.04 Oe was 18 cps, χ' in arbitrary units. Some data points are omitted for clarity.

composition which metallographic analysis showed were composed of almost equal amounts of two phases. These transitions are shown in Fig. 2(a).

In Fig. 1 we have also included more complete temperature data for the 10% $GdRu_2$ sample. It is seen that the peak in χ' corresponds to the point where superconductivity starts to become important. In all of the samples that we measured, including the Bell Laboratory samples, the peak in χ' was due to the beginning of diamagnetic (superconducting) shielding. The samples were measured below 4.2°K, except for the 10% alloy which was also investigated above 4.2°K. In view of this observation we believe that the peaks which Hein, Falge, Matthias, and Corenzwit[5] observed and interpreted as Curie points are actually indications of where superconducting diamagnetism starts. We have superimposed a dc field on two samples which showed a peak in χ'. The measurements on one of these samples are shown in Fig. 2(b). We found that the peak was smaller in a magnetic field and could be completely removed with a field of 600 Oe. As the fields involved are much too

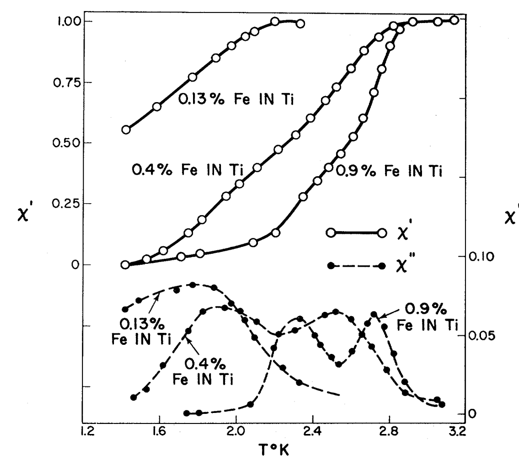

FIG. 3. Zero-field transitions in Ti–Fe alloys. Frequency of ac field of 0.04 Oe was 18 cps. Both χ' and χ'' are in the same arbitrary units, $\chi' = 0$ "superconducting," $\chi' < 1$ diamagnetic.

small to saturate paramagnetic spins, we believe that the sample must be ferromagnetic in this region. The data of Hein *et al.* also show this saturation when they apply a field of 150 Oe.

The peaks in χ'', together with data that indicate complex metallurgical structure in these compounds, suggest that superconductivity is occurring in some interstitial phase in a multiphase sample. However, the suggestion of Matthias and Suhl[6] that superconductivity develops in domain walls and finally forms a superconducting "sponge" remains a possibility, since this type of mechanism would probably lead to a large χ'' peak in the transition region.

[5] R. A. Hein, R. L. Falge, Jr., B. T. Matthias, and E. Corenzwit, Phys. Rev. Letters **2**, 500 (1959).
[6] B. T. Matthias and H. Suhl, Phys. Rev. Letters **4**, 51 (1960).

FE AND RU IN Ti

In this system we find that the addition of small amounts of iron to Ti appears to raise T_c more than a comparable amount of Ru. However, from the nature of the zero-field ac transitions we doubt whether these transitions are truly indicative of a bulk superconductor. We have come to this conclusion because of the large values of χ'' and the observation that the ballistic transitions do not coincide with the ac transitions. In Fig. 3 we show some of the ac transitions. In the 0.13% alloy we found that the ac transition was not complete by 1.3°K and that there was no trace of a ballistic transition. All these observations are explained by filaments of some other superconducting phase such as the β phase, as suggested by Cape.[7] X-ray analysis, to date, has been done on two samples. The major phase in these samples was hcp Ti–Fe. Since we did not observe lines from any other phase of Ti–Fe, we estimate that there must be less than 3% of any other phase.

Although there is little doubt that the transitions we have observed are not bulk phenomena, we have not disproved the existence of a bulk transition at some lower temperature. In view of the work of Cape and Hake[8] on Mn in Fe, in which they found no specific-heat transition in hcp Ti–Mn, it appears likely that there is no unusually high bulk transition temperature in pure hcp Ti–Fe. Preliminary work by Cape[7] and Morin[9] on this system also leads to this conclusion.

ACKNOWLEDGMENTS

We wish to thank Dr. B. T. Matthias, Dr. R. A. Hein, Dr. G. F. Dresselhaus, Dr. R. M. Meservey, Dr. C. E. Chase, and Dr. S. H. Autler for valuable discussions and Dr. Matthias and Mrs. V. B. Compton for making available to us the Bell Laboratory's samples and x-ray data. We would also like to thank E. B. Owens for spectrographic analysis of the samples and Miss M. C. Finn for measuring the lattice parameters.

[7] J. A. Cape, Superconductivity and Localized Magnetic States in Ti–Mn Alloys (to be published).

[8] J. A. Cape and R. R. Hake, Bull. Am. Phys. Soc. **8**, 192 (1963).

[9] See reference to F. J. Morin in Ref. 7.

Discussion 27

FERRELL: I think it might be pertinent to report that Fulde has completed an investigation of the coexistence of ferromagnetic ordering with superconductivity. What has been found is that the two can actually coexist together if we imagine that we have impurities which force spin orientation of some of the electrons. The superconducting ordering can be present even though there is an excess of electron spin. This is a strong field effect, a strong perturbation. It is different from the sort of excess spin that Schrieffer and Cooper consider when they discuss the Knight shift, a weak field effect. There is no real contradiction between having the ferromagnetic impurities lined up exerting a strong field, polarizing some of the electrons, and the rest of the electrons establishing a superconductive coherence.

GORTER: I would like to point out that it doesn't seem very easy to obtain a considerable increase in χ'' for a regular mixture of superconducting and normal regions. Of course you are quite right saying that χ'' will increase. But, it would be difficult to get it very much larger, let us say, by a factor of 10, compared with the normal substance. On the other hand, if you have a sort of sponge structure, then you may have flux creep or flux jumps which could give a large effect.

M. STRONGIN, *Massachusetts Institute of Technology:* Well we know that in some cases we observe a very large χ'' peak and yet we don't observe a ballistic transition until we are through the peak. This seems to exclude the possibility of a connected sponge structure, at temperatures above the peak; the filaments must be unconnected at this point.

MATTHIAS: There has been a lot of talk about the beta phase in Ti with 1%, a 10th %, a 100th % of iron. Has anybody ever seen it? As far as I know no metallurgical technique that has been devised yet has ever seen it. So I don't believe it. The second question I have is, could you get a χ'' if you would have a gradient of the concentration, which you undoubtedly do have as everything else does?

STRONGIN: I don't see why you would get a χ'' peak in any case where you have a Meissner effect.

MATTHIAS: Because you have different transition temperatures; and you certainly don't have a Meissner effect.

STRONGIN: However, if the concentration gradient occurred as superconducting filaments, then you would get it. If it occurred very gradually over the whole sample and exhibited bulk diamagnetism then I would say you wouldn't get a χ'' peak.

MATTHIAS: Do you get a χ'' in Nb?

STRONGIN: Yes, but we don't get it in Ta.

MATTHIAS: If you get it in pure niobium, the whole argument is somewhat pointless. Or do you have filaments (of what?) in pure niobium?

MAXWELL: There is nothing mysterious about the χ'' peak. It occurs in normal conductors. If you take any normal conductor and cool it down to a low enough temperature to make this kind of measurement, you observe a peak if the conductivity becomes high enough. This is an ordinary electrodynamic skin effect. The thing which makes it distinctive in the superconductors is the fact that it occurs over a very small temperature interval. The only model which can explain this is the presence of fine inclusions which don't exhibit a Meissner effect but which do simulate a rapidly increasing normal conductivity; that is, you have a distribution of fine filaments in a normal matrix and this looks like, on a coarse scale, a metal whose normal conductivity is increasing very rapidly. We have some rather striking evidence that is the correct model for this case. We have looked at some lead–tin alloys, solid solution alloys, where first of all the transition is frequency dependent. The higher the frequency at which you make your measurement the higher the apparent transition temperature; this is because frequency and conductivity are interchangeable in this mechanism. If you make the measurements by a ballistic galvanometer technique the transition will occur about 0.02°K degrees lower than the measurement at 18 cps. Finally on the same alloys Shiffman, Cochran, and Garber have made specific heat measurements and find that the transition occurs at a temperature still lower than that determined by the ballistic galvanometer. So the only reasonable explanation is that you have a distribution of filaments which show up first in the ac technique, next in the ballistic technique when they close, and finally at some lower temperature the bulk matrix goes superconducting which is what specific heat measurement shows.

COLES: Dr. Park will be presenting detailed comparison of magnetization curves and ac transition for Sn–In alloys which show effects quite similar to those mentioned by Dr. Maxwell.

T. H. GEBALLE, *Bell Telephone Laboratories:* With respect to Maxwell's comment on the transition temperatures being different when measured different ways, we have data on 1% Fe in Ti. The ac transition and the heat capacity transition as measured by Phillips at Berkeley occur over the same temperature interval. There is no direct evidence for the existence of any beta phase.

Superconductivity under Pressure

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and
E. CORENZWIT and T. GEBALLE
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The effect of pressure p on the critical field H_c of superconductors has been extensively investigated experimentally, and the general features are well understood. It is found that $\partial H_c/\partial p$ depends in a simple way upon the shape of the critical field curve and upon the pressure derivatives of T_c and of the normal state electronic specific heat.

The pressure dependence of the electronic specific heat is a function of the sensitivity of the electronic band structure to volume changes, and is independent of the superconductive properties of the metal. The pressure dependence of T_c, on the other hand, is a characteristic of the mechanism of superconductivity, and should be predictable from the theory of superconductivity.

An examination of the well-known expression

$$T_c = 0.85\,\theta_D \exp\left[-1/N(0)V\right] \qquad (1)$$

for the transition temperature given by Bardeen, Cooper, and Schrieffer shows that the volume dependence of T_c is a function of the volume dependences of the Debye temperature θ, of the electronic density of states at the Fermi surface $N(0)$, and of the interaction parameter V.

The volume dependence of θ is given by the Grüneisen constant γ_G, and the volume dependence of $N(0)V$ has been shown by Rohrer[1] to obey a remarkably simple empirical law in superconductors which are not transition metals or rare earths. In the metals for which data were available to Rohrer (In, Sn, Hg, Pb, Al) he found that

$$\partial \ln N(0)V/\partial \ln v = 2.5 \pm 0.5\,. \qquad (2)$$

Thallium, which is exceedingly anisotropic in its properties, was found to be an exception, however.

It was also found that this simple relation broke down for the transition metals for which the pressure dependence was known, and we have pointed out[2,3] that this failure is in some way connected with the absence of an isotope effect in osmium and ruthenium noticed by Geballe, Matthias, Hull, and Corenzwit,[4] and by Geballe and Matthias.[5]

The nature of this connection remains uncertain, however, and we have thought it useful to collect pressure effect data on additional metals in order to help establish its nature. The form of the expression obtained by differentiation of (1) with respect to volume makes it particularly desirable to examine other metals with small values of T_c/θ.

We have recently investigated the change in tran-

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[2] K. Andres, J. L. Olsen, and H. Rohrer, IBM J. Res. Develop. **6**, 84 (1962).

[3] E. Bucher and J. L. Olsen, *Proceedings of the 8th International Conference on Low Temperature Physics, 1962.*

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