

for  $\Delta\gamma$ ,  $\Delta\chi$ , and  $A$  at low concentrations from the Lederer and Mills theory which are in good agreement with the experimental value. The  $\rho^*/\rho$  ratio seems quite reasonable.<sup>3,18,19</sup> Another fact seems to support the theory of the localized enhancements.<sup>15,16</sup> Although the mean increase of the susceptibility is high, the moment of the Fe impurities does not change with Ni concentration. This can be understood only by a localized increase of  $\chi$  in the neighborhood of the Ni atoms.

We could obtain some data for the coefficient of the  $T^3$  term of the specific heat, in spite of the small value of the ratio  $\beta T^3/\gamma T$  even at 3°K. Although further investigations are under way to lower the error in  $\beta$ , we can already say that there is a steady increase of the calculated Debye temperature  $\Theta_D$  with concentration; but our results do not determine whether it is a new  $\beta T^3$  term or whether it is a real variation of  $\Theta_D$ .

For high concentrations,  $\Theta_D$  falls off again and at 10% it is approximately the same as for our pure Pd ( $235 \pm 8^\circ\text{K}$ ). This behavior cannot be explained by a mass effect but rather by the magnetic fluctuations or perhaps by a phonon-paramagnon coupling.<sup>20</sup>

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#### THERMAL AND MAGNETIC DEGRADATION OF THE QUASIBOUND STATE IN DILUTE MAGNETIC COPPER-CHROMIUM ALLOYS\*

M. D. Daybell and W. A. Steyert

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

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Recent theories of the low-temperature electron state in dilute alloys of magnetic transition-metal atoms in simple metallic hosts have treated the scattering of itinerant electrons as predominantly *s* wave.<sup>1-3</sup> For this reason, the increase in resistivity with decreasing tem-

perature as the low-temperature state is formed is limited to approximately one *s*-wave unitarity limit, or about 0.38 nΩ cm per (at.) ppm impurity in copper. Within the framework of these theories, there has also been quite a bit of recent interest in the behavior of the vari-

ous properties of suitable alloys in a magnetic field large enough to destroy this state.<sup>4,5</sup> We report resistivity and magnetoresistivity measurements, on a new system found to have a convenient Kondo temperature  $T_K$ , which indicate that these theories should be modified to accommodate a large amount of scattering of higher conduction-electron partial waves, most probably  $d$  waves.<sup>2,6</sup> In the Cu(Cr) alloy studied, the magnetoresistivity below  $T_K$  is almost completely saturated by the fields used, so that magnetoresistivity results are now available for this one system over nearly the entire field and temperature range of theoretical interest.

The spherical alloy samples used were cast from high-purity copper mixed with the appropriate amount of a master alloy, Cu plus 0.5% Cr, and were chemically etched before use. Similarly prepared pure Cu samples had residual resistance ratios of about 700 and showed no resistance minima. The samples were suspended below a He<sup>3</sup>-He<sup>4</sup> dilution refrigerator and their resistivities were measured using an eddy current technique.<sup>7</sup> The first measurements, made on a 50- and a 112-ppm sample in zero field, showed the presence of impurity-impurity interaction effects as displayed in Fig. 1 (i.e., the impurity contribution to the resistivity per ppm chromium differed at low temperatures for these two concentrations).

For this reason, the 12- and 28-ppm (a) samples were prepared (from a second master alloy) and studied, with sample 28 ppm (a) inside a 6.35-cm-i.d. superconducting solenoid capable of producing 27 kOe; the results of the zero-field measurements are shown in Fig. 1. The solder used to mount these samples caused a small, spurious, low-field effect in these runs. This effect was eliminated by removing the solder, boring a small hole through the sample, and remounting it using nylon screws. The resulting sample, now designated 28 ppm (b), had essentially the same zero-field resistivity as 28 ppm (a) (cf. Fig. 1). Its resistance in magnetic fields up to 25.8 kOe and temperatures down to 70 mdeg K is shown in Fig. 2.

Zero-field resistivity ( $\rho_0$ ) measurements show the characteristic flattening out at very low temperatures expected for the quasibound state. (The resistivity of a pure-copper control sample has been subtracted in all data presented in this paper.) The suppression of the specific resistivity by impurity-impurity inter-

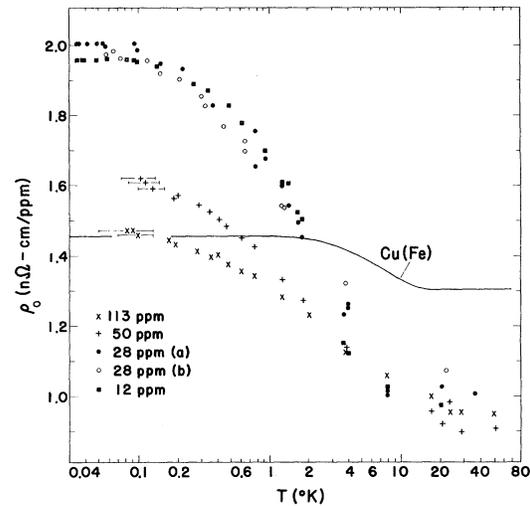


FIG. 1. Impurity contribution to electrical resistivity per at. ppm chromium in copper in zero magnetic field. In this report measurements are uncertain to  $\pm 0.01$  n $\Omega$  cm/ppm and temperature errors are negligible, except where shown. Absolute error in resistivity per ppm is approximately 10%, resulting primarily from uncertainties in impurity concentration. Note the small change in resistivity with temperature for a given sample below 0.1 and above 10°K. Symbols (a) and (b) denote runs on the same sample with slightly different geometries. The smaller resistivity change occurring over a smaller temperature range in the Cu-Fe system is illustrated [M. D. Daybell and W. A. Steyert, Phys. Rev. Letters **18**, 398 (1967)].

action effects appears in the two more concentrated alloys, but is clearly absent in the two more dilute alloys. Several features of the low-concentration results should be noted. First, the resistivity step height is about 2.4 s-wave unitarity limits. In addition, it occurs over a temperature range of about two and a half decades, which approaches the theoretically predicted spread more closely than the approximately one-and-a-half-decade range found<sup>8</sup> in Cu(Fe), shown in Fig. 1 for comparison purposes. Between 30 and 300°K,  $\rho_0$  in Cu(Cr) is known to vary less than 0.015 n $\Omega$  cm/ppm,<sup>9</sup> so that it is essentially flat in this region. The high-temperature resistivity is less in the present alloy, indicating less ordinary potential scattering, a result which is consistent with its different temperature behavior and the small thermoelectric power of Cu(Cr) compared with Cu(Fe).<sup>3,10,11</sup> Copper chromium is thus presumably a purer example of the quasibound state phenomenon than copper iron, although less is presently known

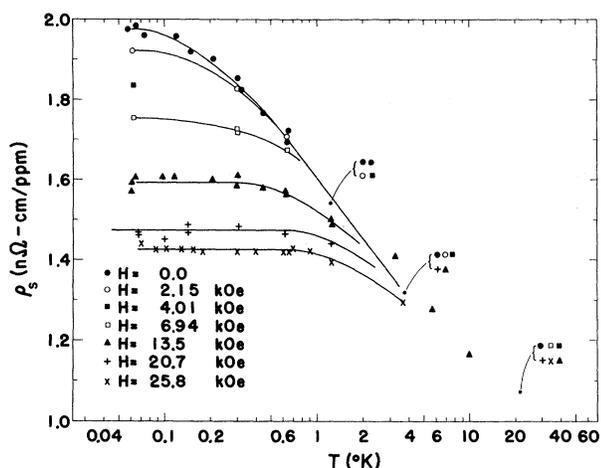


FIG. 2. Impurity contribution to electrical resistivity per at. ppm chromium for various magnetic fields  $H$  for sample 28 ppm (b). The resistivities have been corrected for the normal positive magnetoresistivity measured at  $T = 21.5^\circ\text{K}$ , by subtracting 0.018, 0.029, 0.057, 0.131, 0.207, and 0.255  $\text{n}\Omega\text{ cm/ppm}$  from the  $\rho$ 's measured at 2.15, 4.02, 6.92, 13.5, 20.7, and 25.8 kOe, respectively. The extreme flatness of the resistivity curve at 20.7 kOe was also shown in measurements made on sample 28 (a) where  $\rho_S$  was found to vary less than 0.015  $\text{n}\Omega\text{ cm/ppm}$  between 0.045 and 0.6 $^\circ\text{K}$ .

about its experimental properties. It is also a promising candidate for epr work,<sup>12</sup> unlike Cu(Fe). Its  $T = 0^\circ\text{K}$  resistivity is about 5  $s$ -wave unitarity limits, which would, in a simple picture of Schrieffer's,<sup>6</sup> be consistent with the large number of unpaired localized  $3-d$  electrons to be expected for a chromium impurity. The few magnetization data available<sup>13</sup> seem to indicate that the high-temperature moment of the chromium impurity corresponds to a spin value of approximately  $S = \frac{3}{2}$ .

The resistivity in a magnetic field (Fig. 2) is still quite field dependent at fields much greater than would be required to saturate the magnetoresistivity arising from the bare moment of the impurity alone (for  $g = 2$  and  $S = \frac{3}{2}$ , saturation would be essentially complete at  $T = 0.1^\circ\text{K}$  for  $H = 3$  kOe). Perhaps the most interesting (and, insofar as we know, unexplained) feature of the high-field data is that the resistance becomes temperature independent, and at much higher temperatures in high fields than in zero field. The saturation value, incidentally, is about one  $s$ -wave unitarity limit above the high-temperature limit of  $\rho_0$ .

The relative magnetoresistivity, which is the difference between the zero-field resistiv-

ity  $\rho_0$  and the resistivity in a field (corrected for the temperature-independent positive magnetoresistivity of the alloy)  $\rho_S$ , divided by  $\rho_0$ , is plotted versus  $H/(T + \theta)$  in Fig. 3, with  $\theta = 0.44^\circ\text{K}$ . It is seen to be a universal function of this parameter over considerably more than a decade in temperature. Moreover, at  $T = 0.07^\circ\text{K}$  this function is nearly saturated for fields of about 30 kOe. Existing theoretical<sup>5,14</sup> and experimental<sup>15,16</sup> work would indicate that, at least in the region where the quasibound state is absent or not fully formed,  $-\Delta\rho_S/\rho_0$  should vary as  $M^2$ , where  $M$  is the magnetization of the impurity. Dworin<sup>17</sup> has suggested that, at least for some of the results in copper-iron alloys,  $M$  could be written in the form  $M = aB_S(H/(T + \theta))$ , where  $B_S$  is the Brillouin function for spin  $s$  and  $g = 2$ . In copper iron, susceptibility measurements<sup>18</sup> indicate that although  $\theta = T_K$  for  $T$  below  $T_K$ ,  $\theta$  may be<sup>19</sup> more like  $2T_K$  for  $T$  significantly greater than  $T_K$ . There is some interest then in whether the data of Fig. 3 can be fitted with a curve of the form  $[aB_S(H/(T + \theta))]^2$ . This definitely cannot be done if  $\theta$  is taken to

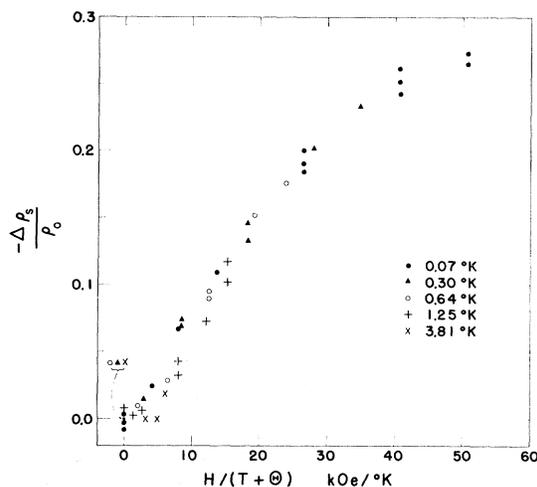


FIG. 3. Spin magnetoresistivity divided by zero-field impurity resistivity for copper +28 ppm (at.) chromium alloy versus  $H/(T + \theta)$  for various temperatures.  $\theta = 0.44^\circ\text{K}$ . The  $0.07^\circ\text{K}$  data can be approximately represented by the square of a  $g = 2$  spin- $\frac{3}{2}$  Brillouin function of  $H/(T + 1.05)$ . As shown, all of the data can be well represented by a single function of  $H/(T + 0.44^\circ\text{K})$ , but this function is definitely not the square of a  $g = 2$  Brillouin function of this argument. In the abscissa units of the figure, a magnetoresistance resulting entirely from the alignment of the bare free spin of the impurities would saturate below 3 kOe/ $^\circ\text{K}$ . Thus the behavior of the magnetoresistance is profoundly influenced by the Kondo effect below a characteristic temperature of between 0.4 and 1.1 $^\circ\text{K}$ .

be temperature independent. However, the  $T = 0.07^\circ\text{K}$  data alone are fit quite well by  $-\Delta\rho_S / \rho_0 = 0.28B\frac{3}{2}(H/(T+\theta))$ , with  $g = 2$  and  $\theta = 1.05 \pm 0.1^\circ\text{K}$ . Another possible form for  $M(H)$  at  $T \ll T_K$  has been given by Nam and Woo.<sup>4</sup> To fit the higher-temperature data, it would be necessary to let  $\theta$  increase with temperature, as happens in Cu(Fe). A more detailed understanding of whether the behavior of the magnetoresistance is simply related to  $M^2$  awaits suitable low-temperature measurements of the magnetization of very dilute Cu(Cr) alloys, and/or the results of theoretical calculations currently in progress. The present data do, however, indicate that  $T_K$  is between 0.4 and 0.9°K and that Cu(Cr) is a nearly ideal system for study of the quasibound state phenomenon. These results show that the  $d$ -wave scattering must be taken into account in any comprehensive theory of the Kondo effect.

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## SUPERCONDUCTIVITY OF RHENIUM AND SOME RHENIUM-OSMIUM ALLOYS AT HIGH PRESSURE\*

C. W. Chu, T. F. Smith,<sup>†</sup> and W. E. Gardner<sup>‡</sup>  
 Institute for the Study of Matter, Department of Physics,  
 University of California, San Diego, La Jolla, California  
 (Received 20 July 1967)

We have measured the pressure dependence of the superconducting transition temperature ( $T_c$ ) of single crystal and polycrystal samples of rhenium and a number of Re-Os solid solutions. In contrast to the nearly linear dependence of  $T_c$  on pressure observed at low pressures for the majority of superconductors, the  $T_c$  of rhenium exhibits an anomalous behavior under pressure. This behavior was rapidly destroyed by the addition of small amounts of Os (>0.2 at.%). We attribute this unusual behavior of  $T_c$  under pressure to a change of the Fermi-surface topology of the type proposed by Lifshitz.<sup>1</sup> We find  $T_c = 1.694 \pm 0.002^\circ\text{K}$  at atmospheric pressure which is in excellent agreement with the values reported by Hulm and Goodman<sup>2</sup> and Blanpain,<sup>3</sup> and we find that at low pressures  $\partial T_c / \partial P = (-2.3 \pm 0.1) \times 10^{-6} \text{ }^\circ\text{K bar}^{-1}$ , a value which is a little larger than

that reported by Olsen *et al.*<sup>4</sup>

Measurements were made on samples cut from Materials Research Corporation (MRC) Grade 1 (zone-refined, 99.9 wt% purity, with major impurities given in ppm by weight as Fe 3.0, Ni 0.3, Nb 1.2, Mo 4.0, Ta 3.0, and W 15.0) polycrystalline and single-crystal Re. Now the sharpness of the superconducting transition in Re is extremely sensitive to plastic deformation and internal strain.<sup>5</sup> Thus samples cut directly from the "as received" material had extremely broad transitions, starting as high as 3°K, with a sharp step at ~1.7°K. An accurate determination of the pressure dependence of  $T_c$  would be impossible with such broad transitions and, therefore, it was necessary to reduce considerably the width of these initial transitions. This was achieved by annealing the rhenium sample in an induction