Susceptibility and Resistivity Studies of Localized Iron Moments in Copper*

M. D. DAYBELL AND W. A. STEYERT

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

(Received 25 October 1967)

Susceptibility measurements in fields from a few Oe to 1 kOe at temperatures down to 40 m°K show that the moment on the iron site is completely compensated at temperatures far below the Kondo temperature, at least at the high-field values. Correlation of these results with Mössbauer measurements reveals new information about the behavior of the low-temperature state formed in these alloys. The experimental technique used is discussed in detail. Some other properties of the copper-iron system are reviewed.

I. INTRODUCTION

PROGRESS in the theory of the anomalous exchange scattering by localized magnetic moments in dilute alloys containing transition-metal solutes has been rapid since it was originated by Kondo[1] in 1964 to explain the resistivity minimum phenomenon seen in these materials.[2] Most prominent among the features of the emerging theoretical picture is the gradual formation of a new conduction electron-impurity "quasibound state"[3] as the temperature is lowered below a certain temperature T_K, the Kondo (or Kondo-Suhl-Abrikosov) temperature.[4-8]

Only quite recently have experiments designed to satisfy the fairly stringent requirements necessary to test the more sophisticated theories been carried out.[9-13] A preliminary report of the present work[11] identified for the first time an alloy, Cu(Fe), in which the expected saturation of the residual resistivity below the resistivity minimum appeared in conjunction with the predicted large reduction of the impurity's magnetic moment. An important feature of the resistivity data is that they clearly established that the alloys were dilute enough that impurity-impurity interactions could not be responsible for the results. Other parameters of this system were soon examined by other workers.[9,10,14] Another system, Au(V), which apparently exhibits many of the properties of the quasibound state has been discovered by Kume.[12,13] Evidence that this state occurs in many other alloys, and over a wide range of temperatures, has recently been collected and reviewed.[2]

New results on the temperature and magnetic field dependence of the susceptibility of Cu(Fe) alloys in the concentration range from 54 to 330 at. ppm (parts per million) are presented here, along with the earlier resistivity data and a discussion of several of the measured properties of this system in the light of recent theoretical ideas. Some general observations are made on the areas where improvements in the theory are needed.

II. EXPERIMENTAL

To study the quasibound state in copper-iron it was necessary to make high-resolution resistivity and susceptibility measurements on extremely pure oxygen-free alloys from above 40°K down into the tens of millidegrees range. Samples were prepared by vacuum induction melting, and were cooled by a He^3–He^4 dilution refrigerator. Bulk samples were used, and their properties were measured from outside the millidegree cold space by an especially developed eddy-current mutual-inductance bridge.[15]

Sample Preparation

American Smelting and Refining Company 99.999+% pure copper was melted together with reagent-grade iron powder in a small high-purity alumina crucible using a vacuum induction furnace. Wedges of the 0.5% iron master alloy thus obtained, together with the desired amount of additional copper,

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] J. Kondo, Progr. Theoret. Phys. (Kyoto) **32**, 37 (1964).

[2] For a recent bibliography and review see, e.g., M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. (to be published).

[3] Y. Nagaoka, Progr. Theoret. Phys. (Kyoto) **37**, 13 (1967); Phys. Rev. **138**, A1112 (1965).

[4] H. Suhl and D. Wong, Physics **3**, 17 (1967).

[5] H. Suhl, Phys. Rev. **138**, A515 (1965); Physics **2**, 39 (1965); Phys. Rev. **141**, 483 (1966).

[6] A. A. Abrikosov, Physics **2**, 5 (1965).

[7] K. Yosida, Phys. Rev. **147**, 223 (1966); Progr. Theoret. Phys. (Kyoto) **36**, 875 (1966).

[8] P. E. Bloomfield and D. R. Hamann, Phys. Rev, **164**, 856 (1967).

[9] R. B. Frankel, N. A. Blum, B. B. Schwartz, and D. J. Kim, Phys. Rev. Letters **18**, 1051 (1967).

[10] M. A. Jensen, A. J. Heeger, L. B. Welsh, and G. Gladstone, Phys. Rev. Letters **18**, 997 (1967).

[11] M. D. Daybell and W. A. Steyert, Phys. Rev. Letters **18**, 398 (1967).

[12] K. Kume, J. Phys. Soc. Japan **22**, 1116 (1967); **22**, 1309 (1967); Phys. Letters **24A**, 743 (1967); also (private communication).

[13] M. D. Daybell, D. L. Kohlstedt, and W. A. Steyert, Solid State Commun. **5**, 871 (1967).

[14] C. M. Hurd, Phys. Rev. Letters **18**, 1127 (1967).

[15] M. D. Daybell, Rev. Sci. Instr. **38**, 1412 (1967).

were then placed in a mold made of Union Carbide type AUC high-purity graphite. The crucible was lined with an alumina paste made of Norton fused alumina #900F milled to about 1 μm and suspended in distilled water. The mold had previously been outgassed in the furnace. The filled mold was heated to about 1300°C for about 20 min, then the molten alloy was cooled slowly though its melting point, and the furnace was turned off. About an hour later, the vacuum system was opened and the sample removed. The resistivity samples were cast into 11-mm-o.d. spheres in two-piece molds, while the mold for the susceptibility samples produced a flat billet about 7 mm×20 mm×50 mm. The billet was sliced lengthwise into strips from 1.0 mm to 1.5 mm thick to form the laminations of these samples. It was necessary to use a 5-mm-o.d. by 25-mm-long fill hole for the spherical molds to avoid surface-tension effects which would otherwise lead to voids in the sample. Each mold was topped by an integral small funnel-like cup which held the initial charge.

The gettering action of the graphite at high temperatures helped minimize oxygen contamination problems, while the alumina coating prevented the iron used from forming carbides with the graphite. Both resistivity samples and the 110- and 145-ppm susceptibility samples were made from the same master, and another piece of this master was kept for chemical analysis. A second master was used for the 330-ppm alloy, and part of this sample was later diluted further to make the 54-ppm alloy. A pure-copper resistivity sample made in the same way as the dilute alloys showed no resistivity minimum, and thus contained less than 1-ppm Fe. The residual resistance of a slab from each susceptibility sample was measured to verify the calculated alloy concentrations.

Mutual-Inductance Bridge

Both the resistivity and the susceptibility measurements were made with a mutual-inductance bridge designed to make possible precise determinations of both the real and imaginary parts of a mutual inductance containing a metallic sample. The resistivity measurements utilize the fact that the eddy-current problem for a spherical conductor can be solved exactly. Alternating current susceptibility measurements are made in the normal way, except that the alloys must be laminated to reduce the eddy currents to a small residual effect that can then be easily corrected for by extrapolating to zero-frequency measurements made at several bridge frequencies from 2 to 30 Hz. To minimize heating of the sample and simplify bridge design, a good low-noise phase-lock amplifier was used as the source and detector for the bridge.[15] In this way, power dissipation in the alloy could be kept below a nanowatt, even at 2 Hz, which was quite necessary.

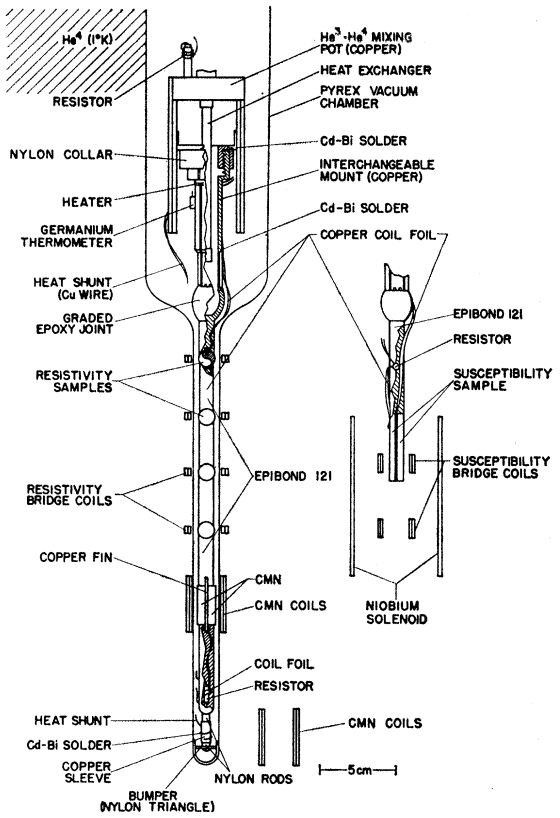

FIG. 1. Experimental arrangement for resistivity measurements for the 63 ppm and pure-Cu samples (left) and susceptibility measurements on the 54- and 145-ppm samples (right). Not shown are the arrangements for a separate resistivity run on the 22-ppm-Cu(Fe) sphere, and the arrangements for the zero-field susceptibility measurements on the 110- and 330-ppm samples where the sample resistor was mounted below the sample.

The absence of leads to the sample from warm temperatures down into the 40 mdeg temperature region was highly desirable from a cryogenic standpoint. One of the most significant advantages of the eddy-current technique for dilute-alloy work is that the low resistivities encountered can be determined in bulk samples. The uncertainties caused by the strains and the solvent oxidation and precipitation introduced in drawing the alloys into the long, fine wires needed in more conventional techniques are avoided. An accuracy of better than 1% can be obtained with this technique, and its precision can be considerably better than 0.3%.

Cryogenics

The samples were located in a vacuum space, and were suspended below a He^3–He^4 dilution refrigerator. The Pyrex vacuum container and copper measuring coils surrounding the samples were immersed in the 1.1°K helium bath. A number of resistivity samples were measured in the same experimental run as shown in Fig. 1. After the interchangeable sample mount was

assembled as described below, it was screwed on to the dilution-pot experiment connector.[16] Four vertical slits in the threaded portion of the mount allowed a nylon collar to force the threads together very tightly upon cooling,[17] providing good thermal contact between the dilution pot and the copper portion of the sample holder. The upper sample, in turn, was mechanically and thermally attached to the sample holder via a molded epoxy[18] support with a coil foil of about 100 insulated 80-μm wires imbedded in it. The upper end of these were stripped and soldered to the copper portion of the mount with Cd–Bi eutectic solder for good thermal contact.[19] The wires were attached to the top spherical sample via a pressure contact using a 0-80 brass screw threaded into the top of the sample along the vertical axis. A similar pressure contact from the bottom of the sample to the coil foil provided cooling for the next lower sphere, and so on, until finally the cerium–magnesium-nitrate mounting plate and lower resistance thermometer were connected. Because of the length of the sample structure and the small (1.5 mm) clearance between the samples and the glass envelope at 1 to 1.2°K, the spacer on the bottom was necessary to guarantee centering. The heat leak through the spacer was shunted directly to the refrigerator via several 0.13-mm 99.999% copper wires. A calibrated 100-Ω Speer grade 1002 $\frac{1}{2}$-W resistor measured the refrigerator temperature, while a similar resistor measured the gradient developed along the sample chain. Normal eddy-current heating of the sample created a measured gradient of 0.02°K at the lowest temperatures. For the coldest data point the measuring current was decreased and the gradient lowered to 0.007°K. The cerium–magnesium-nitrate susceptibility provided a temperature calibration for the lowest resistor, which was also used in later experiments as one of the primary thermometers. Above 4°K a calibrated germanium thermometer attached to the sample holder was used.

For the simultaneous measurement of the 63-ppm sample and two pure-copper spheres[20] the thermometry between 4 and 20°K utilized the Speer resistors which were calibrated at 20°K in liquid hydrogen. Above 20°K the resistors and the resistivity of the pure-copper samples served to give approximate temperature values. A later run to measure the 22-ppm sample was made without the use of the pure-Cu reference samples, the thermometer being the calibrated germanium resistance thermometer.

For the Cu(Fe) susceptibility measurements a similar arrangement was used. The insulated coil foil from the copper portion of the sample holder was squeezed for about 2 mm of its length between the upper ends of the copper slabs. This end of the slabs was potted in epoxy to make a good thermal and mechanical bond. In the case of the 110-ppm sample of Ref. 11 and the 330-ppm sample the resistor to monitor the gradient was mounted below the sample, with the compensating coil mounted on a short piece of Pyrex tube in the 1°K bath alongside the glass vacuum container. No superconducting Nb magnet was used. For the 54- and 145-ppm samples the compensating coil was mounted directly below the sample coil as in Fig. 1 and symmetrically placed in the Nb magnet.[21] It was not now permissible to mount the resistor below the sample because it would be in the compensating coil. Therefore the resistor to monitor the temperature gradient was placed between the sample and refrigerator, but thermally connected only to the sample by coil foils pressed against the sample slabs. This coil foil was wrapped and glued around the resistor body.

The possibility of minute quantities of contaminants with a temperature-dependent susceptibility in the in the sample, on the sample or on the sample supports near the coils can strongly affect the results of these measurements. The precautions against such contamination were as follows:

(1) While the preliminary measurements of Ref. 11 used 5-μm Mylar insulation between slabs, the later samples were spaced in such a way that this was unnecessary.

(2) The coils were short, about $\frac{1}{3}$ the sample length; thus they could be kept away from the support structure, particularly on the 54- and 145-ppm samples which had the epoxy on only one end. In this case, the coils were placed $\frac{2}{3}$ of the way down the sample as shown.

(3) The coils were as small in radius as possible with only 1-mm clearance between the samples and the glass. This allowed a good magnetic filling factor with a minimum sensitivity to materials outside the coils.

(4) The samples were etched, rinsed, and dried quickly with alcohol immediately before assembly into support structure, and were rinsed and dried again immediately before putting the glass vacuum envelope in place.

[16] This gold-plated copper piece was soldered to the copper sections which extend down from the dilution pot. The 6 cm² area of Cd-Bi solder between the close-fitting machined surfaces should not form a thermal impedance to cooling (Ref. 19); at the same time the connector could be moved up or down to accommodate various experiments.

[17] This technique was brought to our attention by Professor R. J. Sarwinski.

[18] It was formed of Epibond 121 (Furnace Plastics Co., Los Angeles) in paraffin molds, with a graded joint of Epibond 121 to Epibond 104 to the copper mount.

[19] W. A. Steyert, Rev. Sci. Instr. **38**, 964 (1967).

[20] A pure-copper sample melted and molded as the doped samples and a copper sample machined directly from the 99.999% copper rod were both measured. Both gave a temperature-independent residual resistivity of 1.6 nΩ cm. The fourth sample was a Cd–Bi sphere whose superconducting transition was measured and reported in Ref. 19.

[21] It was necessary to drive this magnet with a constant current source to avoid a zero shift in the very sensitive susceptibility measurements. A 200 V, 1.5 A regulated dc supply with 100 Ω in series was used.

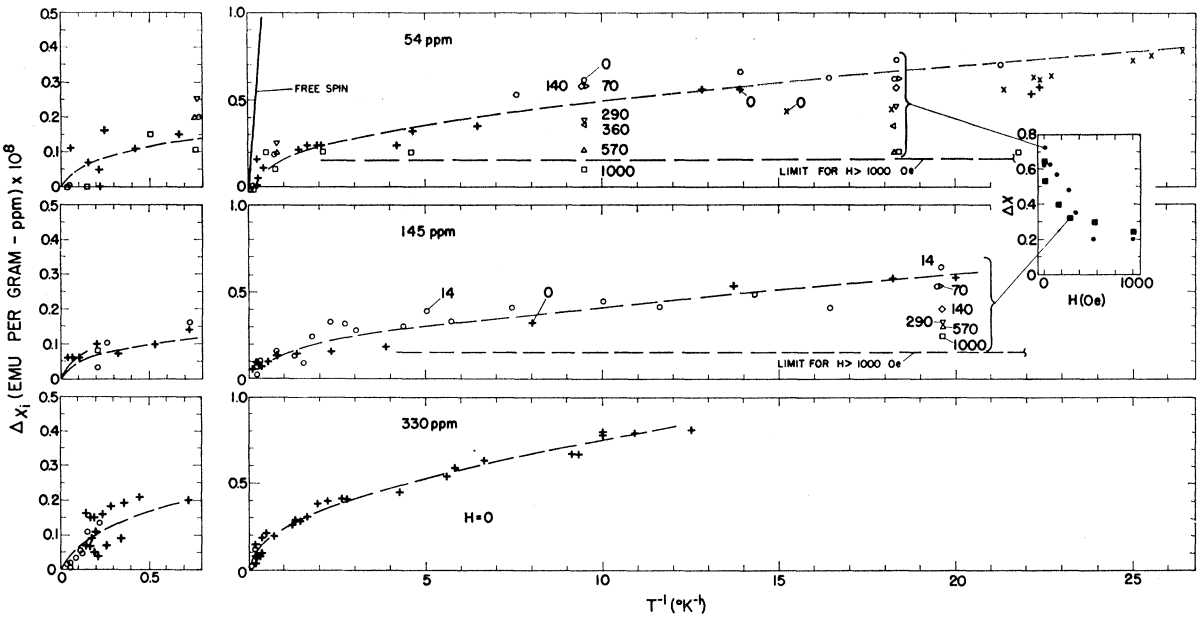

FIG. 2. Incremental susceptibility per gram of alloy per atomic ppm versus reciprocal temperature for various concentrations of Fe in Cu. The applied field (in Oe) is shown in the figure. The open symbols, X's, and crosses are each separate runs with separately determined zeros. The free spin would be characteristic of $\mu_{\text{eff}}=3.7\ \mu_B$ as implied by Hurd's high temperature data. A $T^{-1/2}$ fit to the zero field data is shown. The inset shows the field dependence of the $\Delta\chi_i$ data. The limiting high-field susceptibility is estimated as $0.15\pm 0.05\times10^{-8}$ emu/g at. ppm below 0.5°K (i.e., 0.095 emu/mole Fe.) The comparatively large ac susceptibility measured in zero field may be a magnetic contamination effect. Hurd's high-temperature data appears as the short extra curve in the center left plot. Estimated uncertainties in sample concentrations and geometrical factors are about 10%.

(5) Since Pyrex is paramagnetic, the compensating and sample coils were around a similar piece of glass. It was found that changing the bath temperature from 1.1 to 1.4°K (while holding that of the sample, refrigerator etc., unchanged) caused almost no change in the coil balance.

(6) Nevertheless, the bath temperature was held constant to within 0.1°K during an experimental sequence.

(7) The necessary precautions were taken to avoid oxygen contamination in either the N_2 or He baths.

After the bath was cooled to 1.1°K measurements were made as the sample temperature was varied from 1.1°K to about 10°K using the heater (a bifilament of 1 m of 0.06-mm Manganin wire; cf. Fig. 1). The refrigerator was turned on and measurements made as the sample cooled. The heater was then used again and measurements taken as the sample warmed to the 30°K region in order to check for zero shifts during the course of the run. The zero of the incremental susceptibility was determined by making the data above 5°K agree with Hurd's results. At the lowest temperatures on the 145-ppm sample it was necessary to decrease the measuring signal amplitude and the resulting small zero shift was determined and adjusted for in the results.

III. RESULTS

Susceptibility

The results of the incremental susceptibility measurements are shown in Fig. 2. The most striking feature is the much lower magnetic moment than would be expected from an effective moment at $3.7\mu_B$ (3.7 Bohr magnetons). This effective moment is arrived at from Hurd's high-temperature measurements and is consistant with a g factor (g) of 1.9 and a spin (S) of $\frac{3}{2}$ (saturation moment $\mu_s=gS\mu_B=2.85\mu_B$). The dramatic decrease of the measured ac susceptibility at fields of several hundred Oe could be due to a contaminant which has a temperature-dependent, easily saturable moment. In this series the decrease tended to scale with Fe concentration. This scaling is different from that of the 110-ppm sample of Ref. 11, whose slabs were separated with Mylar.

In any event, the zero-field data are fitted quite well by $\Delta\chi_i=\alpha T^{-0.5}$ over the 2 decade range where our data are meaningful. For the 330-ppm data, which are the most precise, the uncertainty in the 0.5 exponent is less than 10%. The coefficient α is 0.155×10^{-8} at 54 ppm, 0.13×10^{-8} at 145 ppm, and 0.235×10^{-8} at 330 ppm (in emu $°K^{1/2}$/g ppm).

With a magnetic field of greater than 1000 Oe the

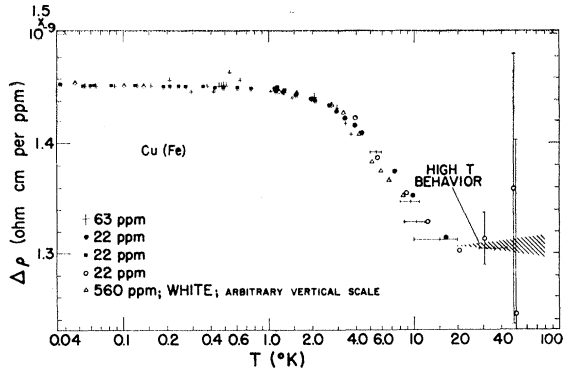

FIG. 3. Impurity contribution to the electrical resistivity/at. ppm iron impurity in copper from Ref. 11. Except where error bars appear, errors on open circles and crosses are ±0.01 nΩ cm/ppm, errors on filled symbols are 0.001 nΩ cm/ppm, and temperature errors are negligible. Absolute error in the resistivity per ppm is approximately 10%, resulting primarily from uncertainties in the impurity concentration. The high-temperature behavior is deduced from Ref. 23 and unpublished results of the present authors.

54- and 145-ppm data below about 1°K are temperature-independent with $\Delta\chi_i=(0.15\pm0.05)\times10^{-8}$ emu/g ppm$=0.095\pm0.03$ emu/mole Fe. If we take $\Delta\chi_i=N_0\mu_{\rm eff}^2/3kT_K$ with $N_0=$Avogadro's number, $\mu_{\rm eff}=3.7\mu_B$, and k is Boltzmann's constant, then T_K is 18°K. In 1000-Oe fields, the impurity susceptibility is down by a factor of 350 from the free-spin value at our lowest temperatures,[22] showing almost complete spin compensation well below T_K with only a temperature-independent paramagnetism remaining.

Resistivity

The impurity contribution to electrical resistivity $\Delta\rho$, shown in Fig. 3 for the 63-ppm sample, is the difference between the resistivities of the alloy and the pure-copper castings. A later run measured the resistance of the 22-ppm material without the use of pure Cu reference samples. The large uncertainties with this sample at high temperatures are due to the uncertainty in the amount of lattice scattering to subtract. (At 50°K, for example, a 1°K uncertainty in the temperature gives rise to the uncertainties in $\Delta\rho$ shown). The unsubtracted data are given in Table I. Domenicali and Christenson's[23] data show $\Delta\rho_i$ to change about 0.01 nΩ cm/ppm between 30 and 80°K for their 500- to 3000-ppm Cu(Fe) alloys. We have made resistivity studies on the 145- and 330-ppm χ samples which show that $\Delta\rho_i$ is changed by less than 0.04 nΩ cm/ppm between 20 and 75°K. These results are indicated by the shaded area in Fig. 3.

[22] Static nuclear susceptibilities at our lowest temperatures would be comparable to our high-field susceptibilities. The long nuclear relaxation time reduces the ac susceptibility to a very small fraction of this static value. Because of this, the nuclear susceptibility of the host is not taken into account in these measurements.

[23] C. A. Domenicali and E. L. Christenson, J. Appl. Phys. **32**, 2450 (1961).

IV. DISCUSSION

The theoretical picture of the quasibound state or "exchange-scattering" problem is currently in a stage of rapid development, and it is inadvisable to take the details of this picture too seriously as yet. With this caveat, a comparison of the general features of the experimental properties of the Cu(Fe) system with various current theoretical predictions is, in fact, quite encouraging.

Nearly all of the detailed theoretical calculations dealing with the low-temperature behavior of the interaction of the localized electron magnetic moment of a magnetic impurity with the moments of the conduction electrons of the host metal start from the exchange-

TABLE I. Resistivity of Cu alloy containing fraction of iron impurity indicated. The 1.62 nΩ cm residual resistivity of the pure-Cu sample has not been subtracted from these measured values.

63 at. ppm		22 at. ppm	
T	ρ(nΩ cm)	T	ρ(nΩ cm)
55 m°K	93.5	37 m°K	33.59
65 m°K	93.5	53 m°K	33.56
87 m°K	93.5	60 m°K	33.56
125 m°K	93.5	64 m°K	33.56
155 m°K	93.5	83 m°K	33.56
210 m°K	93.8	120 m°K	33.56
295 m°K	93.1	190 m°K	33.54
380 m°K	93.5	210 m°K	33.54
420 m°K	93.1	240 m°K	33.54
460 m°K	93.5	270 m°K	33.54
475 m°K	93.5	355 m°K	33.51
495 m°K	93.5	430 m°K	33.51
515 m°K	93.5	480 m°K	33.51
535 m°K	94.2	610 m°K	33.51
645 m°K	93.8	760 m°K	33.49
1.03°K	93.1	1.1°K	33.49
1.46°K	92.8	1.13°K	33.44
2.07°K	92.8	1.15°K	33.51
2.96°K	92.2	1.26°K	33.41
		1.53°K	33.36
3.4±0.2°K	91.3	1.97°K	33.28
3.7±0.3°K	90.7	2.09°K	33.24
5.5±0.5	89.7	2.60°K	33.15
9.5±1.5°K	86.9	2.91°K	33.04
10.3±1.7°K	85.8	3.33°K	32.91
15 ±5	84.8	3.90°K	32.77
36 ±8	89.0	3.95°K	32.91
		4.40°K	32.60
		5.60°K	32.12
		7.35°K	31.86
		8.90°K	31.42
		9.80°K	31.36
		12.3°K	30.85
		16.5°K	30.80
		21.5°K	31.33
		30.8±0.5°K	37.39
		48.2±1°K	76.02
		50.2±1°K	79.99

interaction Hamiltonian used by Kondo:

$$H_{\text{exch}} = -J\mathbf{S}\cdot\mathbf{s}, \qquad J<0. \tag{1}$$

Here S is the spin of the impurity, s is the spin density of the conduction electrons at the impurity site times an atomic volume, and the coupling constant J has been defined according to current usage. The status of the exchange Hamiltonian as an approximation to earlier, more detailed models[24] of the localized moment itself has been pointed out elsewhere.[25,26]

By solving the set of approximate equations of motion for the many-body Green's functions derived with this Hamiltonian by Nagaoka,[3] expressions have been obtained for the resistivity,[27] susceptibility,[27] and specific heat of dilute magnetic alloys,[8] at least if $S=\frac{1}{2}$.

Another current approach to the exchange-scattering problem utilizing essentially the same Hamiltonian is to use an adaptation of dispersion-theoretic methods from elementary-particle theory.[4,5] While the structure of this approach is now thought to be very close to that of the Green's-function approach,[28] the computational work done with this technique[4] has the advantage that the apparently important effect of the ordinary *potential* scattering (Suhl and Wong's V) on the exchange-scattering mechanism has been included from the start. Also, this theory is presented for values of S greater than $\frac{1}{2}$, although the published numerical results are restricted to $S=\frac{1}{2}$. With these two additional parameters, it is possible to come much closer to fitting the experimental resistivity and thermopower measurements that can be done using present Green's-function calculations. No dispersion-theoretic results are available for either the specific heat or the susceptibility.

It is important to point out that in order to make meaningful comparisons between these theories, which ignore effects due to the thermal properties of the host lattice, it usually is necessary to assume that it is legitimate to subtract the contribution of the host material from the experimental result. This seems to work reasonably well,[11–13] but is hard to justify *a priori*. Another practical problem is that, in systems where the quasibound state occurs at low temperatures so that the corrections for the host are small, S will probably of necessity be large, since a low Kondo temperature seems to be associated with a large impurity spin.[2] Thus a direct comparison of the predictions of models in which S is restricted to $S=\frac{1}{2}$ with experiments is difficult.

Because it is a relatively simple alloy with a Kondo temperature in the middle of a convenient experimental range, the copper-iron system is currently the best choice available for comparison with theoretical predictions. Each of several of its macroscopic properties will be discussed separately. For convenience, the Green's-function approach and the dispersion-theoretic approach will be denoted by I and II, respectively.

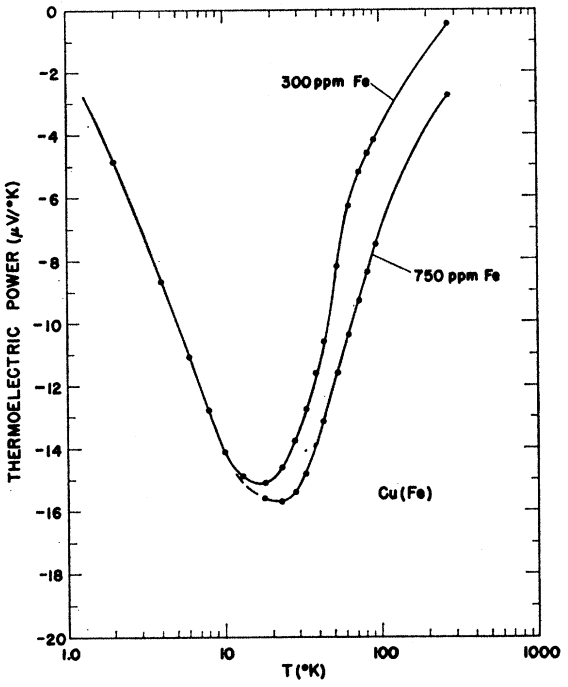

FIG. 4. Absolute thermoelectric power of copper alloys containing a few hundred ppm (at.) of iron. Results at 1000 ppm are similar to the 750-ppm curve. The magnitude of the peak decreases for larger or smaller concentrations of iron. At 750 and 1000 ppm, the peak occurs at 21°K. Data are from G. Borelius, W. H. Keesom, C. H. Johansson, and J. O. Linde, Leiden Commun. **217e** (1932); Suppl. **70a** (1932).

Resistivity. A characteristic feature of both I and II is that the residual resistivity of a dilute magnetic alloy should rise near the Kondo temperature approximately as $-\ln T$ from its high-temperature value to its $T=0$ value, reflecting the gradual breakup of the quasibound state. For $S=\frac{1}{2}$, $V=0$, this rise should correspond to one s-wave unitary limit in the scattering cross section, giving a resistivity change per atomic ppm of $4\pi\hbar/(ne^2k_F)$, where n is the conduction-electron density, e is the electronic charge, and k_F is the Fermi wave number. For Cu(Fe), this is approximately 0.38 nΩ cm/ppm. In II, this value is modified by the effect of the potential V. The temperature range over which this transition takes place varies from as many as eight decades, in I and in II if V is small, to as few as three decades for the largest V values used in II. The middle of the transition occurs at T_K in I, but well below T_K in II if V is large. Experimentally, a step only one and one-half decades wide with a height of 0.40 unitary limits, centered at about 6.1°K occurs.

According to a particularly simple scheme suggested

[24] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[25] J. R. Schrieffer and P. A. Wolff, Phys. Rev. **149**, 491 (1966); J. A. Appelbaum, K. H. Bennemann, and J. W. Garland, *ibid.* **161**, 583 (1967).
[26] J. R. Schrieffer, J. Appl. Phys. **38**, 1143 (1967).
[27] D. R. Hamann, Phys. Rev. **158**, 570 (1967).
[28] S. D. Silverstein and C. B. Duke, Phys. Rev. Letters **18**, 695 (1967); D. S. Falk and M. Fowler, Phys. Rev. **158**, 567 (1967).

by Schrieffer[26] for taking into account the d-orbital degeneracy present in an actual magnetic impurity such as iron, the *total* $T=0$°K resistivity introduced by an impurity of spin S should saturate at $2S$ times the unitarity limit for a d wave of a given magnetic quantum number m. For plane-wave conduction-electron states, this is numerically equal to $2S$ times the s-wave unitarity limit, or, for copper, $0.38\times 2S$ nΩ cm/ppm. For Cu(Fe), this limit is about 1.2 nΩ cm/ppm if S is approximately $\frac{3}{2}$, or about 17% less than the present experimental result. In Cu(Fe), most of this limit has already been used up by ordinary temperature-independent potential scattering before the system has been cooled below the Kondo temperature. The extra 0.26 n Ω cm/ppm resistivity observed experimentally may be due to potential scattering of partial waves other than d waves.

Thermoelectric power. A roughly Gaussian peak appears near T_K in the thermoelectric-power-versus-ln$T$ plots of II. The sign of this peak is determined by that of V. A negative peak of the correct general form in fact occurs at $T=21$°K although it is only about two decades wide, and thus narrower than those presented in II. These results are shown in Fig. 4 for two iron concentrations low enough that impurity-impurity interactions are not important. The effect of lattice scattering is apparent.

Specific heat. A peak in the excess specific heat per impurity at about one third T_K has been predicted in I, and a peak indeed is seen in the experiments,[29] somewhere between 4.5 and 6°K. The height of the experimental peak is about three times that predicted[8] on the basis of $S=\frac{1}{2}$, which is in agreement with a suggestion based on a model of Schrieffer's,[26] if S is actually $\frac{3}{2}$. The peak is only about one decade wide, however, in contrast to the two-decade width predicted (for $S=\frac{1}{2}$). The measurements do not yet extend to low enough temperatures to indicate clearly whether the predictions that the specific heat should vary as the square root of T as T approaches absolute zero are correct.[8] We are setting up to make this measurement, which also bears on a recent model[30] of the localized moment obtained directly from the Anderson Hamiltonian.[24]

Susceptibility. One of the more interesting questions concerning the properties of the quasibound state is to what extent the spin of the bare localized moment is compensated by the polarization of the itinerent electrons coupled to it by the (antiferromagnetic) exchange interaction. The most obvious effect of this spin compensation should be to decrease the paramagnetic susceptibility of the impurity below its free-spin value as T decreases below T_K. This effect was indeed observed in preliminary measurements on Cu(Fe), reported earlier.[11] Above T_K, the incremental susceptibility per added impurity $\Delta\chi_i$ fits reasonably well a Curie-Weiss law with an effective moment of $\mu_{\text{eff}}=3.68$ Bohr magnetons (corresponding to $S=\frac{3}{2}$ if g is approximately two) and a Curie-Weiss temperature of 32°K.[14] This is not entirely unexpected, since several calculations predict a free-spin paramagnetic susceptibility at high temperatures, and at $T=0$°K, $\Delta\chi_i$ is expected by some authors[31,32] to approach $\mu_{\text{eff}}^2/(3kT_K)$, although none of the present theories connects these two limits. Recent magnetization results[33,34] in the region between that studied by Hurd (above 5°K) and the present ($H=1000$ Oe) work below 1°K show that there is a smooth transition between the two. A simple Curie-Weiss law of Hurd's form does not, therefore, describe the data below about 10°K. There is some reason to believe that the high-temperature value of the Curie-Weiss parameter θ ($=32$°K) is an overestimate of T_K.[2] One expression for $\Delta\chi_i$, given by Hamann,[27] diverges slowly as T approaches 0°K.

The recent suggestion by Anderson[30] that $\Delta\chi_i\propto T^{-1/2}$ at very low temperatures is particularly interesting in the light of the present results.

Use of the ac-bridge technique made it possible to measure the susceptibility of Cu(Fe) in essentially zero field. The rms measuring field at the sample was less than 4 G, while its frequency was approximately 3 Hz. Alloys having a range of iron concentrations from 54 to 330 at./ppm were examined to establish the concentration independence of the incremental susceptibility per impurity. In zero field, the susceptibility obeyed a $T^{-1/2}$ law remarkably well over the entire temperature range from 0.05° to at least 4°K, above which the precision of the data drops rapidly because of the decreasing magnitude of incremental susceptibility.

In order to learn whether a very small amount of magnetic contamination proportional to the added iron impurity were present, possibly in the form of undissolved iron, the dc magnetic field dependence of the ac susceptibility was also measured in two of the samples. It was found that in a field of about 1 kG, the susceptibility flattened out below 0.5°K at a value of $\Delta\chi_i=\mu_{\text{eff}}^2/(3kT_K)$, where $T_K=18$°K if the effective moment is taken as 3.7 Bohr magnetons. The vanishing of the derivative of $\Delta\chi_i$ ($H=1000$ Oe) with respect to $1/T$ implies a large reduction of the localized magnetic moment; within the precision of the data, the moment may be taken to be zero below 0.5°K. Another point worth noting is that at $T^{-1}\approx 19$, $\Delta\chi_i(0)-\Delta\chi_i(H)$ resembles closely the derivative of a Brillouin function

[29] J. P. Franck, F. F. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961); F. Du Chatenier and J. De Nobel, Physica **32**, 1097 (1966).
[30] P. W. Anderson, Phys. Rev. **164**, 352 (1967).
[31] L. Dworin (private communication).
[32] H. Ishii and K. Yosida (unpublished); V. Jaccarino (unpublished).
[33] F. T. Hedgcock, W. B. Muir, T. Raudorf, and R. Szmidt (unpublished).
[34] P. Monod (unpublished).

for $\mu_{\text{eff}}=3.7$ Bohr magnetons, $S=\frac{3}{2}$. This is not true at higher temperatures.

The picture we are left with, then, is that the predictions that $\Delta\chi_i$ goes as $T^{-1/2}$ as $T\to 0$ agree with the experimental results extremely well, but only at very low fields. Unless there is some as yet unexpected mechanism present in the quasibound state, it is hard to see why application of a field of less than 1000 Oe should cause the system to go over into a nearly completely spin-compensated state as is observed. Were it not for the recent $T^{-1/2}$ law predictions, one could with a clear conscience associate the low-field results with the presence of an extremely small concentration of free spins in the form of magnetic contamination and take the high-field results as representing the inherent properties of the Cu(Fe) system. As it is, the possibility that the low-field effect seen is real cannot be ruled out. It is not, incidentally, associated with the magnetic destruction of the quasibound state, which would require a field greater than 100 kOe. An analysis of the "reagent-grade iron" received after the experiments were performed indicated that it contained 0.6% Mn in the iron, rather than "less than 0.1%," as claimed by the supplier. Residual effects from this source could contribute to the small field-dependent susceptibility observed at our lower temperatures.

Mössbauer results. Mössbauer resonance is used to measure the magnetic hyperfine field (H_i) at the Fe impurity nucleus in copper due to the alignment of the moment on the impurity center in an external field, H, while susceptibility measures the magnetization of the impurity center produced by alignment in the external field. Thus Mössbauer and susceptibility measure similar, but not identical, properties of the impurity center. By intercomparing the two measurements we can learn more of the nature of the spin compensation than by studying each individually.

We first examine the Mössbauer results. At high temperatures we know from Hurd's results[14] that the moment on the impurity center behaves like a uncompensated free spin of $\mu_s=gS\mu_B=2.85\mu_B$. The H_i for the fully aligned spin is deduced to be $-80\,000$ Oe.[9] For partially aligned spins at high temperatures $H_i=-80\,000f$ Oe, where f is the fractional spin alignment. In the high-temperature region, Mössbauer experiments show[35] $H_i=-8.4H/T$ Oe; thus

$$H_i=f\times(-80\,000)=-8.4H/T \qquad \mu_s H/kT\ll 1, \tag{2}$$

or

$$f=1.05\times 10^{-4}H/T \qquad (H \text{ in Oe}, T \text{ in } ^\circ\text{K}). \tag{2'}$$

Likewise the magnetization on the sample is due to the alignment of the $2.85\mu_B$; i.e.,

$$\Delta\chi_i H\equiv\langle\mu\rangle N_0=2.85\mu_B f N_0=1.71H/T, \tag{3}$$

$$\langle\mu\rangle=2.85f\mu_B. \tag{3'}$$

The value $1.71/T$ is from Hurd's measurement of $\Delta\chi_i$ at high temperatures. The expectation value of the impurity moment along H is $\langle\mu\rangle$.

Putting in values of Avogadro's number, N_0, and μ_B we also find that

$$f=1.05\times 10^{-4}H/T. \tag{4}$$

That this is consistant with Eq. (2') merely shows that the value of H_{sat} is correctly chosen in the case of high temperatures where complications due to bound-state formation are absent.

Now, let us examine the results for $T<1^\circ$K where the bound state is fully formed. Here,[35]

$$H_i=-0.47H \qquad H<100 \text{ kOe}; \tag{5}$$

but H_i can be considered to be made up of a part due to the fractional alignment f of the localized electrons plus an assumed contribution $H_{\text{comp}}(H,T)$ from the spin-compensation electrons.[36] Thus

$$H_i=(-80\,000)f+H_{\text{comp}}(H,T)=-0.47H. \tag{6}$$

Likewise, the magnetization has a contribution $p_{\text{comp}}(H,T)\mu_B N_0$ due to spin-compensating electron polarization:

$$M=\Delta\chi_i H=0.095H=[2.85f+p_{\text{comp}}(H,T)]\mu_B N_0. \tag{7}$$

Solving Eq. (6) for f and substituting into Eq. (7) we see that

$$0.095H=0.095H+[2.85\times 1.25\times 10^{-5}H_{\text{comp}}(H,T)+p_{\text{comp}}(H,T)]\mu_B N_0 \tag{8}$$

or

$$p_{\text{comp}}(H,T)=-3.57\times 10^{-5}H_{\text{comp}}(H,T). \tag{9}$$

This relation is the same in both sign and magnitude as the relation between H_i and $\langle\mu\rangle$ for the localized electrons on the iron at high temperatures where the bound state has not been formed. [Dividing Eq. (3') by Eq. (2) we see $\langle\mu\rangle=-3.57\times 10^{-4}H_i$.] Thus, taking experimental errors to be about $\pm 30\%$ we can say that either:

(1) p_{comp} and H_{comp} are much smaller than the respective contributions of the uncompensated spins, $2.85f$ and $-80\,000f$ (by at least a factor of 3), or

(2) If p_{comp} and H_{comp} are the order of $2.85f$ and

[35] T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. **138**, A467 (1965).

[36] For a detailed discussion of the sources of internal fields at nuclei, see R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

$-80\,000f$, then p_{comp} and H_{comp} are related in about the same way as $\langle\mu\rangle$ and H_i for the localized electrons (to within about 30%).

The result of this analysis implies that either,

(1) p_{comp} and H_{comp} are small, and the large reduction of the effective moment as observed is brought about by the failure of the $2.85\mu_B$ moment to align in an external field as a free spin would. This might result from a quantum-mechanical admixture of spin-up and spin-down wave functions to form the singlet state, or

(2) below 1°K there is a compensating moment p_{comp} developed that is equal and opposite to the original $2.85\mu_B$ to within 5%. The character of this compensation moment is very much like that of the original $2.85\mu_B$ moment since it produces the same field at the nucleus, per Bohr magneton.

Nuclear magnetic resonance. One other way of probing the magnetization of the iron impurity is by observing the increase in the magnetic resonance linewidth ΔH of the host copper nuclei caused by the local moment. In principle, this shift should be proportional to the magnetization, and an analysis directly analogous to that applied to the Mössbauer data can be performed, using available data.[10,37] Here, possibly because of measurement and interpretation difficulties, the cancellation of the term linear in H that occurred in the Mössbauer case [Eq. (8)] is only about $\frac{2}{3}$ complete. If this lack of cancellation is real, it would imply that the part of the excess linewidth attributable to the spin-compensating electron polarization at very low temperatures is not related to the fractional alignment of the localized electron by the same expression that relates the excess linewidth at high temperatures to the fractional alignment of the high-temperature moment.

V. SYNOPSIS

The evidence from the available experiments is that the qualitative features of the quasibound state are well described by current theories, but many of the detailed predictions of these calculations are only semiquantitatively correct. Kondo temperatures obtained from different types of measurements on the well studied copper-iron system range from somewhere around 10°K from the resistivity results, using Suhl's curves, through the 15–18°K obtained from specific-heat results and the $T=0$°K susceptibility limit, and the 21°K thermopower number, on up to the 32°K obtained by assuming that the Curie temperature needed to fit the high-temperature susceptibility data is equal to T_K. The problem here may simply be the lack of a detailed calculation of all four experimentally measurable properties using a single approach, including the effects of $S\neq\frac{1}{2}$, and of sufficiently large V.

A second discrepancy which runs consistently through these comparisons is that the number of decades of temperature necessary to complete the transition from the low-temperature behavior to that at temperatures above T_K is about a factor of 2 lower than the number of decades predicted by the theory. This is true for the resistivity, the specific heat, and the thermopower, and may simply be a result of the neglect of effects arising at large S and/or large V. A smaller theoretical width for this transition region would make it easier to determine T_K accurately. Because T_K is related to J by an equation of the form $T_K=D\exp(-N/J\rho)$, where ρ/N is the density of states of conduction electrons of a single-spin direction, per atom, and $2D$ is of the order of the conduction band width, high accuracy for T_K is not needed for an accurate determination of J. Taking $T_K=15$°K, $D=5$ eV, and $\rho/N=0.16$ eV, $J=0.8$ eV. This way of defining J differs somewhat from that of Eq. (1), since the above expression for T_K, though convenient, is only approximate.[4]

Complete understanding of the quasibound state awaits a more detailed theoretical and experimental exploration of its microscopic properties, but quite a few of its macroscopic features now appear to be in agreement with the current theoretical picture.

Note added in proof. In order to further investigate the magnetic contamination problem, zero-field ac susceptibility measurements have been carried out on a 140 ppm Cu(Fe) sample. While this sample was prepared with spectroscopic standard Fe containing less than 3 ppm Mn, it nevertheless showed an incremental susceptibility equal to $0.15\times10^{-8}T^{-1/2}$. Thus the larger zero-field susceptibility cannot be attributed to a magnetic impurity in the iron dopant.

ACKNOWLEDGMENTS

Communication with Dr. Hedgcock, Dr. Anderson, Dr. Dworin, Dr. Maley, and Dr. Suhl, as well as preprints from several authors have been extremely helpful in this work. The expert assistance of Don Hull in preparing the samples, and of Robert Cole, Dr. William Pratt, Don Clinton, and David Kohlstedt in the fabrication and execution of these experiments was invaluable.

[37] T. Sugawara, J. Phys. Soc. (Japan) **14**, 643 (1959).