generally for any state of the form $\hat{y}f(\vec{n})$, where f is a scalar function (e.g., an $l=3$ spherical harmonic).

In writing down the state (c) as the "best" BW state we have argued as follows. In zero external field the dipole energy of the BW state is minimized if we start from the configuration $\vec{d}=\vec{n}$ and then rotate $\vec{d}(\vec{n})$ through the angle $\cos^{-1}(-\frac{1}{4})$ about an arbitrary axis. We have assumed that in a finite field we should choose this axis to be the z axis, since the number of $S_z=0$ pairs is slightly less than the number of $S_z=\pm 1$ pairs and it is therefore more important to correlate the latter. Then we see that the resultant state does not show a "transverse" shift but does show a large longitudinal shift. Hence it is possible that ^{3}He B is in a BW phase,[4] and we can test this hypothesis by a longitudinal NMR experiment.

We conclude: (1) The phenomenon of shifting of the resonance(s) is quite insensitive to whether or not there exists a $\hat{k}_\chi$ in Anderson's[4] sense, or a finite total angular momentum; thus, contrary to Ref. 4, a shift will occur for longitudinal polarization (even for the BW state) and will in no case tend to zero as $\vec{\mathcal{H}}_0 \to 0$. (2) The shift cannot be ascribed to an effective internal field lying in the xy plane, since at low external fields the motion of $\vec{S}'$ is more nearly linear than circular [see Eq. (12)]. (3) Existing experimental data on ^{3}He A probably cannot determine the nature of the configuration unambiguously, but lower-field data will go a long way towards doing so. (4) ^{3}He B may be in a BW state, and this can be tested by longitudinal NMR experiments.

I am very grateful to Bob Richardson, Dave Lee, and Bill Truscott for their interest in this work and for helpful discussions of the experimental situation; to Vinay Ambegaokar, Phil Anderson, Bill Brinkman, G. Stare, and (especially) David Mermin for numerous valuable comments and suggestions; to Joe Serene for many helpful discussions and a careful check of a vital numerical factor; to Jean Fuchs for her patience with my handwriting; and to the Laboratory of Atomic and Solid State Physics at Cornell University for hospitality during a most enjoyable and stimulating stay.

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[1]D. D. Osheroff, W. J. Gully, R. C. Richardson, and D. M. Lee, Phys. Rev. Lett. 29, 920 (1972).

[2]A. J. Leggett, Phys. Rev. Lett. 29, 1227 (1972), and 30, 411(E) (1973).

[3]R. Balian and N. R. Werthamer, Phys. Rev. 131, 1553 (1963).

[4]P. W. Anderson, Phys. Rev. Lett. 30, 368 (1973).

[5]A much fuller treatment will be given elsewhere, including discussion of the physical significence of $\vec{T}(\vec{n})$, limits of applicability of the theory, predicted spectral weights, a detailed comparison with experiment, and the effects of "quasiparticle" renormalization.

[6]P. W. Anderson and W. F. Brinkman, Phys. Rev. Lett. 30, 1108 (1973).

[7]D. D. Osheroff, Ph. D. thesis, Cornell University, 1972 (unpublished).

[8]R. C. Richardson, private communication.

[9]The numerical factor F quoted in Ref. 2, and also the ratio $\frac{64}{13}$ quoted in footnote 13 there, are wrong because of a computational error. The correct values may be deduced from the C_i quoted above.

New Mössbauer-Effect Measurements on the System Fe:*Cu*

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High-field ($H \leq 60$ kG) and low-temperature ($T \geq 25$ mdeg K) Mössbauer-effect measurements of the Kondo system Fe:*Cu* are reported. The comparison of these results with bulk susceptibility data leads to a polarization, of antiferromagnetic sign, of the electron gas in the Kondo state.

The true nature of the Kondo effect is far from being understood; this is so for the theoretical[1] as well as for the experimental[2] side of the problem. For simplicity one may, as far as the experimental situation is concerned, divide the measurements into macroscopic and microscopic ones. For the macroscopic the situation is reasonably simple. The properties like resistivity,

thermopower, susceptibility, etc., show "low"-temperature ($T \approx T_K$) anomalies like the minimum of the resistivity. These anomalies are characteristic for the occurence of the Kondo effect, though their exact temperature dependence may not always be the same for every system under consideration. The situation is far more complex with respect to the microscopic measurements. First of all there are much fewer data available and, secondly, these methods give contradictory results. The situation can very well be described with respect to the system Fe:*Cu*, on which we shall also present data in this communication. The Mössbauer-effect[3,4] measurements on Fe:*Cu* of Frankel *et al.*[3] showed for the first time the disappearance of the magnetic moment on a microscopic scale. A correlation of these data with macroscopic susceptibility measurements by Heeger[5] seemed to indicate a considerable ferromagnetic polarization in the electron gas in the Kondo state. About one half of the total susceptibility was thought to reside in the electron gas as a result of that analysis. NMR measurements on the Cu resonance of this system were then used to determine the temperature and field dependence of this polarization cloud ("quasiparticle"): Fields of 60 kOe and temperatures of 16°K were needed for its destruction. In view of more elaborate susceptibility measurements[6] this analysis seems to be questionable. In addition, neutron-diffraction measurements by Stassis and Shull[7] showed, though admittedly with a considerable error, that the total and local susceptibility agreed also in the Kondo state. Thus on the basis of this experiment, only a small polarization could be present in the electron gas. On the other hand, Potts and Welsh[8] have extended the NMR measurement, obtaining experimental results similar to those of Heeger and of Golibersuch and Heeger,[2,5] although in considerably more detail. It should be kept in mind that NMR measures via the linewidth the induced oscillatory spin polarization well away from the impurity and not the net spin polarization. A comparison with the Mössbauer-effect data is therefore not straightforward. Of particular interest in this respect are the NMR measurements on Co:*Cu* ($T_K \approx 500$°K) of Lang *et al.*[9] Although the experiments were performed at really low temperatures ($T = 4.2$°K $\ll T_K$), these authors were able to detect satellites in the Cu spectrum which could be interpreted as produced by the polarization of the electron gas by the Co moments. This interpretation implies that there are moments (on a microscopic scale) on isolated Co ions, even far below the Kondo temperature of $T_K \approx 500$°K. (It is well known that pairs of Co atoms in the Cu matrix have a much smaller Kondo temperature, $T_K \approx 30$°K, and that triples of Co atoms show no Kondo effect at all![10]) This finding is in agreement with the neutron-diffraction measurements on *Cu*:Fe.[7] In addition, this work[9] shows that the arguments used by the NMR workers[5,8] to rule out the possibility that pairs of magnetic ions influence seriously the NMR spectra may not be valid. The theoretical side of the problem has also recently seen some very interesting developments. Anderson and Yuval[11] showed the equivalence of the Kondo problem and the one-dimensional Coulomb gas; using this equivalence they gave arguments that, e.g., the susceptibility remained finite for $T \leq T_K$, in contrast to other earlier theoretical approaches.[1] Schotte and Schotte[12] explored this method numerically and obtained a finite value for the susceptibility for all temperatures. More recently Götze and Schlottman[13] solved that model self-consistently by a perturbation approximation.

The inconclusiveness of the experimental situation as well as the new theoretical developments made it attractive to look into the experimental situation again. Mössbauer-effect experiments have the advantage that they measure directly the local susceptibility which also comes out of the calculations, thus providing a direct comparison. A low-temperature experiment ($T < 1$°K) on the system Fe:*Cu* yields, with moderate magnetic fields, very high H/T ratios. We have therefore performed such an experiment which in brief yielded the following new results: There is indeed a polarization, though small, of antiferromagnetic sign in the electron gas in the Kondo state which vanishes with strong applied fields ($H \approx 100$ kOe) and with increasing temperature ($T \approx 30$°K). The local susceptibility is found to deviate from the Curie-Weiss law at the lowest temperatures, in agreement with theoretical predictions.[11-13]

The Mössbauer experiments were performed in a He^3-He^4 cryostat, which reached temperatures down to 25 mdeg K (with a radioactive source) and fields of up to 60 kG. In order to achieve high counting rates the source and absorber were placed close to each other such that they both experienced the same external field. The spectra in this geometry look slightly more complicated, but evaluation of the relevant data with a computer presents no problem. The source

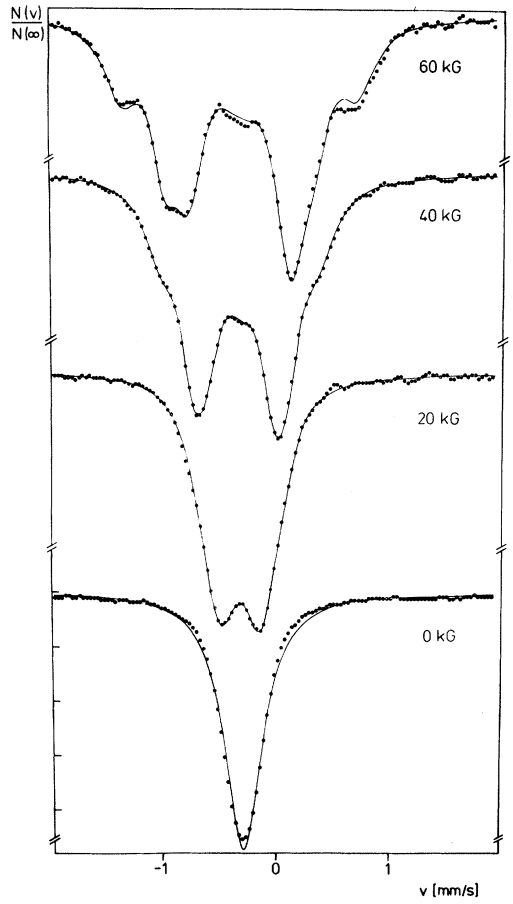

FIG. 1. Mössbauer spectra of Fe:*Cu* at 30 mdeg K for various external fields. The absorber was potassium hexacyanoferrite at 1.3°K in the same external field.

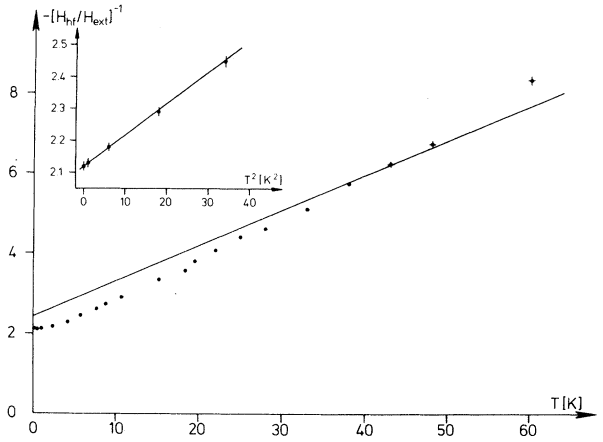

FIG. 2. Reciprocal initial local susceptibility of Fe:*Cu* obtained from Mössbauer experiments. The straight line corresponds to the Curie-Weiss law of the total susceptibility. The inset shows on an expanded scale the low-temperature values as function of T^2.

was about 1 mCi of carrier-free Co^{57} diffused into a Cu foil; the concentration of magnetic ions was estimated to be about 10 ppm. The absorber was potassium hexacyanoferrite enriched in Fe^{57}; it was always kept at 1.3°K, which made it unnecessary to take into account its polarization in the external field. The source was attached directly to the mixing chamber of the He^3-He^4 cryostat. A typical set of spectra at 30 mdeg K for different external fields is shown in Fig. 1. The solid lines are the result of a computer fit from which the internal fields of Fe:*Cu* (from the splitting in the source) and of Co:*Cu* (from the polarization of the spectra) and the applied external field (from the splitting in the absorber) were obtained. The high statistical accuracy of the spectra, as visible from the small scatter of the experimental points, allows the determination of the internal fields at the Fe site with an accuracy of about 1%. The spectra could be measured up to a temperature of 60°K.

The hyperfine field as seen by an isolated Fe ion is a measure of the local susceptibility. As it has been demonstrated that interaction effects can markedly modify the single-ion susceptibility, one has to check first whether the observed data do indeed correspond to it. There are two pieces of evidence that show that interaction effects play no role in our data. First, at all temperatures 25 mdeg K $< T <$ 60°K a linear dependence of the hyperfine field on the external magnetic field (10 kG $\leq H_{ext} \leq$ 60 kG) was observed. From the susceptibility measurements of Tholence and Tournier[6] it is quite obvious that, e.g., at 4.2°K the hyperfine fields of Fe ions which have one nearest neighbor should saturate already in very moderate fields. Secondly, at all temperatures and all fields the spectra could be fitted with the assumption of a single hyperfine field, exhibiting anomalies in its temperature dependence below $T_K \approx 30$°K, thus demonstrating that fields in pairs of ions did not play a role in the experiments. The initial local susceptibility as measured in the present experiment is shown in Fig. 2. It can be seen that it deviates from a straight line at low temperatures and that indeed it can be approximated by a T^2 behavior as suggested by Schotte and Schotte.[12]

In order to see whether there is a polarization in the electron gas, this local susceptibility has to be compared with the total susceptibility as measured in a macroscopic experiment. For this comparison the data of Tholence and Tour-

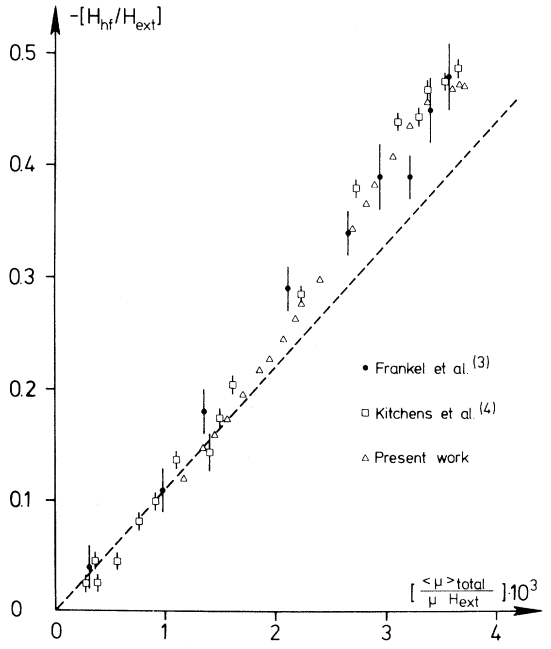

FIG. 3. Initial local susceptibility of Fe:*Cu* obtained from Mössbauer experiment as a function of the total susceptibility, from measurements from Refs. 6 and 14. The straight line gives a saturation hyperfine field of $H_{sat} = -111(3)$ kG for the totally aligned moment.

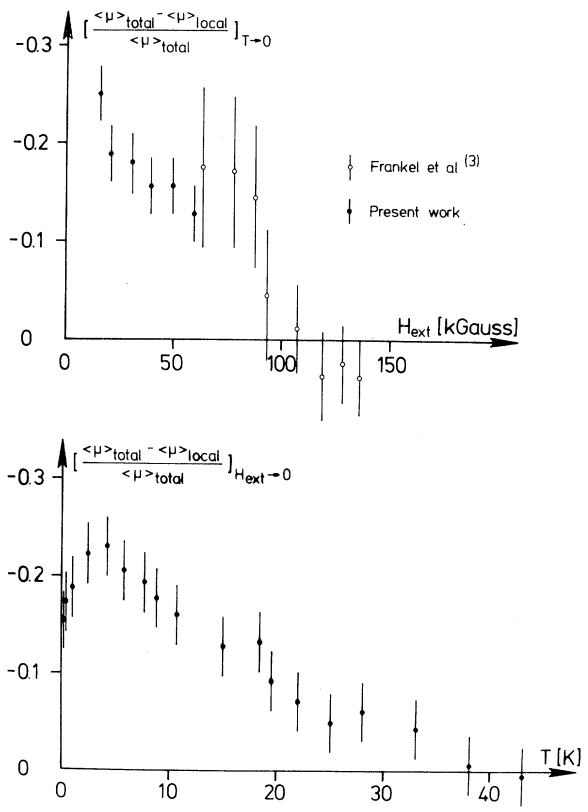

FIG. 4. Relative conduction electron polarization in Fe:*Cu* obtained from Mössbauer experiments and bulk susceptibility measurements as function of external field and temperature.

nier[6] (which are corrected for the contribution due to Fe pairs) and, at higher temperatures, those of Hurd[14] were used. These data can be described by $\chi_{tot} = C/(T+\theta)$ with $\theta = (28 \pm 1)$°K, and C gives a value of $\mu = 2.77(3)\mu_B$ for the moment of Fe:*Cu* with $g = 1.85(2)$ and $s = \frac{3}{2}$. For a meaningful comparison of the local and total susceptibility one has to check whether they contain a temperature-independent orbital contribution[15,16]; this has to be subtracted in order to obtain from the experimental data the pure spin susceptibility. Within the limits of error a fit to the experimental total susceptibility, containing also a temperature-independent term, yielded always a zero constant term. Therefore one can assume that the measured total susceptibility is indeed the spin susceptibility. Using the above function for the total susceptibility, H_{hf}/H_{ext} was plotted as a function of the total susceptibility (Fig. 3). This curve contains also the data of Kitchens, Steyert, and Taylor[4] and Frankel *et al.*[3] which are in agreement with the present data. This procedure of fitting the data has been used successfully by Narath[15,16] to deduce the orbital contribution to the local susceptibility. For $T \to \infty$ the total susceptibility of *Cu*:Fe goes to zero (see above), and if the local susceptibility does contain a temperature-independent orbital contribution this results in a non-zero intercept for $\chi_{tot} \to 0$; since in the present case the high-temperature (low-χ) data give a curve that falls within the limits of error through the origin, it can be concluded that the orbital contribution also for the local susceptibility is negligibly small. Therefore the measured total and local susceptibilities represent the spin susceptibilities. From the high-temperature data we deduce a value of $H_{hf} = -111(3)$ kG for the saturation hyperfine field of the totally aligned spin. The data show unambiguously that at low temperatures (high χ) there is an extra contribution of antiferromagnetic sign to the local susceptibility. This can be seen even better in Fig. 4, where this extra susceptibility is plotted as a function of temperature and as a function of applied field (for $T \approx 0$°K), including $H_{ext} > 60$ kG, the Mössbauer results of Frankel *et al.*[3] Although the errors are still large we think that there is definitely evidence for the ex-

tra susceptibility. This effect can also not be produced by a peculiar field dependence in either of the two measurements. The total susceptibility and the local susceptibility are both linear functions of the external field for $H_{ext} \leq 60$ kG. The polarization in the electron gas obtained in this experiment may have a different cause from that which comes out of the analysis of Heeger.[2,5] Besides the difference in sign as deduced in Refs. 2 and 5, the field and temperature dependences seem to be different; the NMR data give lower values of these variables for the destruction of the polarization cloud although the data on the field dependence of Potts and Welsh[8] are not inconsistent with the present ones if one extrapolates them to very low concentrations. The present values ($H \approx 100$ kG; $T \approx 30$°K) have the advantage of being equal in terms of energy, taking the value of $\mu = 2.8\mu_B$ for Fe:*Cu*.

In conclusion, we have shown that the local susceptibility of the Kondo system *Cu*:Fe follows a temperature dependence as expected on theories following the model of Anderson and Yuval.[11] In addition, we find a small antiferromagnetic polarization of the electron gas in the Kondo state.

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[1]J. Kondo, *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 183.
[2]A. J. Heeger, *Solid State Physics*, edited H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 283.
[3]R. B. Frankel, N. A. Blum, B. B. Schwartz, and D. J. Kim, Phys. Rev. Lett. 18, 1050 (1967).
[4]T. A. Kitchens, W. A. Steyert, and R. D. Taylor, Phys. Rev. 138, A467 (1965).
[5]D. C. Golibersuch and A. J. Heeger, Phys. Rev. 182, 584 (1969).
[6]J. L. Tholence and R. Tournier, Phys. Rev. Lett. 25, 867 (1970).
[7]C. Stassis and C. G. Shull, Phys. Rev. B 5, 1040 (1972).
[8]J. E. Potts and L. B. Welsh, Phys. Rev. B 5, 3421 (1972).
[9]D. V. Lang, J. B. Boyce, D. C. Lo, and C. P. Slichter, Phys. Rev. Lett. 29, 776 (1972).
[10]R. Tournier and A. Blandin, Phys. Rev. Lett. 24, 397 (1970).
[11]P. W. Anderson and G. Yuval, Phys. Rev. Lett. 23, 89 (1969).
[12]K. D. Schotte and U. Schotte, Phys. Rev. B 4, 2228 (1971).
[13]W. Götze and P. Schlottmann, to be published.
[14]C. M. Hurd, J. Phys. Chem. Solids 28, 1345 (1967).
[15]A. Narath, Solid State Commun. 10, 521 (1972).
[16]A. Narath, CRC Crit. Rev. Solid State Sci. 3, 1 (1972).

Direct Evidence for Interstitial-Atom Trapping by Co^{57} Impurities in Aluminum from Mössbauer-Effect Measurements after Low-Temperature Neutron Irradiation

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The Mössbauer effect was used to study the effects of neutron irradiation on aluminum doped with Co^{57}. Annealing between 32 and 70 K after irradiation at 4.6 K induces in the previously single-line Mössbauer source spectrum a new component with small quadrupole splitting, which has an isomer shift of +0.40 mm/sec against the original single line. The new component disappears irreversibly on further annealing between 180 and 250 K. This component is interpreted as being due to interstitials trapped in the immediate proximity of the Co^{57} impurity atoms.

Up to now most studies of radiation damage in metals have been carried out by observing the change in macroscopic solid state properties, such as the electrical resistivity. The Mössbauer effect promises the advantage for such studies in that it gives detailed information about the microscopic properties of defects in the vicinity of Mössbauer atoms. Particular sensitivity for such defects occurs in two special cases: (a) When the excited level of the Mössbauer atom is populated via a nuclear reaction such as thermal-neutron capture or Coulomb excitation, then the atom receives a recoil from the nuclear reaction which can produce lattice defects in its immediate vicinity.[1-4] Such neighboring lattice defects are also produced when the Mössbauer atom is recoil-implanted into a lattice.[5] (b) Alternatively defects can be introduced into the lat-