by Park and McConn.[6] Magneto-optical studies for the identification of bound-exciton spectra, as carried out in CdS[9] and CdSe,[10] would be difficult to make because of a relatively broader nature of the linewidths in this material in contrast to the sharp emission lines observed in CdS and CdSe (half-width 6-10 Å, compared with 0.1 Å). In view of this, the technique reported here is certainly a valuable tool in the identification of emission lines.

In CdS we have studied the intensity variation of the I_2 (4867-Å) line, which is associated with an exciton bound to a neutral donor,[9] as a function of the excitation photon energy. The excitation spectrum for the I_2 line at 4.2°K is shown in Fig. 2. The peaks corresponding to $B(n=1)$ and $A(n=2)$ states are observed. The $A(n=1)$ peak appears as a step near the onset of the I_2 emission. The sucessive maxima in the excitation spectra are separated by the LO-phonon energy of 0.037 ± 0.001 eV from the Γ_5-A exciton (4855 Å). The observation contrasts to that made by Conradi and Haering in that they observed peaks occurring at the excitation energy $E = I_5 + n\hbar\omega_l$.

Thus, both in ZnSe and CdS we observed direct or phonon-assisted excitation of free excitons. These free excitons subsequently give rise to the observed bound-exciton lines. Here we have direct evidence regarding the formation of the bound exciton complexes from phonon-assisted creation of free excitons.

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TRANSITION FROM BOUND TO VIRTUAL 4*f* IMPURITY LEVELS IN METALS*

J. A. Blodgett and C. P. Flynn
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois

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A transition believed to carry 4*f* electrons of Gd from bound to virtual levels in Ag-Al and Cu-Al alloys has been observed by means of the solvent Knight shift.

The 4*f* levels of lanthanide atoms lie much too deep to mix with conduction states in pure rare-earth metals, and it is generally supposed that this holds true for rare-earth impurities in other metals. In this Letter we report measurements of a striking electronic transition in rare-earth impurities as a function of solvent electron density. The transition is believed to take 4*f* electrons from bound to virtual levels with increasing electron density.

Rare-earth impurities in liquid Al cause solvent Knight-shift changes[1] which have the opposite sign, and are too large, to find a comfortable explanation in terms of exchange scattering of conduction states by *f* levels, and the accompanying Ruderman-Kittel-Yosida[2] spin-density oscillations. The observed effects are, however, in good agreement with a hypothesized impurity structure in which *f* sub-bands 0.5 eV wide, split by 1 eV, lie near the Fermi surface.[1] In contrast, recent experiments have shown that *f* scattering causes Knight-shift changes in liquid Cu two orders of magnitude smaller than those in Al.[3] We have therefore investigated the variation of spin-density disturbance with conduction-band width by observing the solvent Knight-shift changes caused by Gd impurities in liquid Ag-Al and Cu-Al alloys as a function of composition.

The experimental values of $\Gamma = K^{-1}dK/dc$ are shown as functions of composition in Fig. 1. Here, K is the solvent Knight shift and c is the Gd concentration. The measurements were performed at about 1100°C. Each Knight shift (Al and Cu in Al-Cu and Al in Al-Ag) shows a sharp

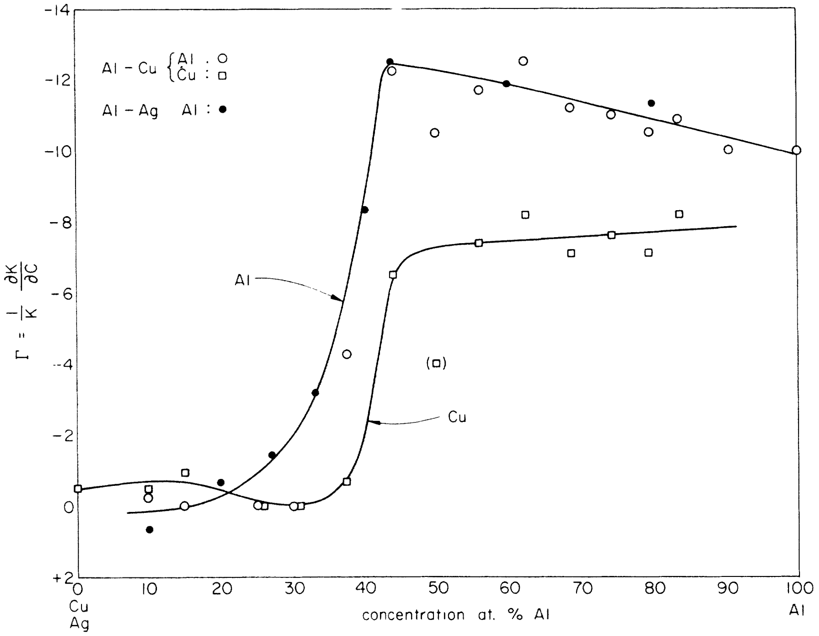

FIG. 1. The fractional Al and Cu Knight-shift changes caused by unit Gd concentration in some CuAl and AgAl alloys.

transition at a composition of ~37% Al. A marked minimum in Gd solubility occurs in the transitional region. The susceptibilities of rare-earth impurities in both pure Cu[3] and pure Al[1] are in good agreement with spin-orbit coupling theory[4] for free ions in the $4f^7$ configuration, as expected for either bound or narrow virtual levels.

Two explanations of the data can be offered, but fortunately the experimental facts appear to exclude one possibility. We could ascribe the abrupt change either to a transition in which bound f levels enter the conduction band as virtual bound f states, or to a valence rearrangement of the ions modifying exchange scattering. The most likely form of valence structure change would be from approximately s^2d in Cu and Ag to s^2p in Al. We can, however, rule out the latter possibility because the results of Ref. 1 (which have since been extended) show that Eu and Gd in Al give rise to spin polarizations which differ only by 10% despite the configurational change from $4f^7 6s^2$ to $4f^7 6s^2p$. It is therefore most unlikely that spin polarization in Al is caused principally by exchange scattering, and consequently the transition cannot be attributed to valence rearrangements. More complicated changes of ion structure are not compatible with the observed susceptibilities.

It is not too unlikely that $4f$ levels could become degenerate with band states in Al. In pure Gd the f band lies ~14 eV below the Fermi surface,[5] whereas in Al and Ag the conduction bands are about 11.5 and 6 eV wide. The discrepancy of 2.5 eV between these numbers for Al cannot be regarded as serious because (a) the estimate for pure Gd is said to be uncertain,[5] (b) the bound states will be broadened by proximity with the band,[6] and (c) most important, the self-consistent Gd cell potential in Al may differ considerably from that in pure Gd. A larger discrepancy exists between the free Gd $4f$ (one electron) energy of ~−21 eV[7] and the combined conduction-band width plus work function of pure Al ~−16 to −17 eV.[8] For Cu and Ag the value is −13 to −14 eV. This comparison, however, ignores all effects of the metallic crystal on the f levels, and the influence of the nearby conduction band may be substantial. The similar effects of Ag and Cu appear to support rigid band arguments.

A sharp transition is to be anticipated because, as the f levels become degenerate with the band bottom, both f and valence states must be drawn from the electron gas, and the self-consistent potential must change abruptly. Virtual f levels are then pushed upwards from the band bottom by the slow variation of f-wave phase shift with k ($\sim k^7$). States bound near the band bottom have been discussed in several articles.[6,9,10]

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LONGITUDINAL MAGNETORESISTANCE OF PURE SINGLE-CRYSTAL COPPER

Alan F. Clark and Robert L. Powell
Cryogenics Division, Institute for Basic Standards, National Bureau of Standards, Boulder, Colorado

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The longitudinal magnetoresistance was measured along the [100] direction of a pure single crystal of copper. The temperature dependence of the saturation ratio, $\rho(B=\text{sat.})/\rho(B=0)$, is given between 4 and 35°K. A limit is placed on the diffusion approximation for small-angle electron scattering and it is suggested that the assumption of a relaxation time or of a mean free path parallel to the velocity is not valid for some types of impurity or low-temperature phonon scattering.

The longitudinal magnetoresistance of metals has been proposed as a means of determining the effective mean-free-path variations upon the Fermi surface.[1] Both Pippard[1] and Klemens and Jackson[2] have formulated expressions for the saturation ratio of the longitudinal magnetoresistance for isotropic scattering and, under the diffusion approximation, for very small angle scattering of electrons.[1,2] Comparison of the saturation ratios for known scattering mechanisms or for known scattering angles yields information regarding the regions of validity of these approximations.

We have measured the longitudinal magnetoresistance between 4 and 35°K along the [100] direction of a pure single crystal of copper whose residual resistance ratio, $\rho_{273\,^\circ\mathrm{K}}/\rho_{4\,^\circ\mathrm{K}}$, is 41 800. The effective electrical purity of the specimen was increased by an oxidation-annealing treatment[3] of a single crystal grown from selected 99.9999% pure copper. After removal of the spark-planing surface damage,[4] the sample was 2 mm × 2 mm × 3 cm and was oriented along the [100] crystal axis to within 0.1 deg. Voltage probes, soldered on the surfaces, were precisely located and confined by 0.1-mm holes in a protective coating of varnish. The voltages were measured using a system with an imprecision of 50 pV. Orientation in the magnetic field was accomplished by observation of the magnetoresistance signals.

The temperature dependence of the saturation ratio, $\rho(B=\text{sat.})/\rho(B=0)$, is shown in Fig. 1. The curve shows the change in ratio from nearly total impurity scattering of the electrons at 4°K to nearly total phonon scattering of the electrons at 35°K. Also indicated is the percentage of phonon scattering determined from a plot of resistivity versus temperature. The low-temperature zero-field measurements were corrected for size effect using the equation of Nordheim[5,6] and a measured $\alpha\rho_B l_B$ on the same piece of copper.[7]

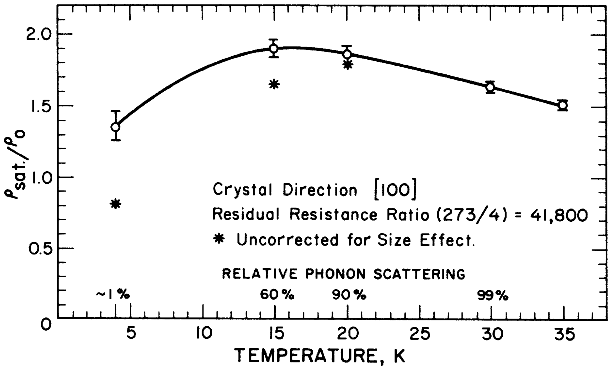

FIG. 1. Longitudinal magnetoresistance saturation ratio for copper.