Observation of NMR of the Formation of Localized Electronic States in an Ionic Liquid Alloy

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^{133}Cs NMR results are reported for liquid Cs-Au alloys ranging from pure Cs to 18% excess Au in the ionic liquid compound CsAu. As one approaches CsAu from the Cs-rich side, a rapid drop in the Knight shift is observed, accompanied by a sharp peak in the nuclear relaxation rate at about 5% excess Cs in CsAu. Analysis of the static and dynamic hyperfine fields shows that the conduction electrons abruptly localize, probably as *F*-center analogs, when the concentration of excess Cs falls below about 7%.

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Several binary alloys of nearly-free-electron-like liquid metals have recently been observed to undergo striking transformations to a nonmetallic state near compositions of simple stoichiometry.[1-3] These "ionic alloys" or "charge transfer insulators"[4] are characterized by large charge transfer and have excited considerable interest.[5-8] One such system, Cs-Au, exhibits a conductivity (found to be ionic[9]) of about 3 $(\Omega\ \mathrm{cm})^{-1}$ at the composition CsAu.[2,10] Studies of the electrical transport properties[2] and magnetic susceptibility[11] suggest that the electrons introduced by small excess metal concentrations in the "salt" CsAu are localized.[12] Little is known, however, about the nature of these localized states or of the conditions under which they are formed.

In this Letter we report the first direct indication of the transition from extended (metallic) to localized states in such a system. Our ^{133}Cs NMR studies show that there exists a well-defined concentration of Cs in CsAu below which the electronic states abruptly become localized. The hyperfine properties of these states indicate that localization occurs in the form of *F*-center analogs rather than as neutral atoms.

Cesium-gold alloy samples were prepared *in situ* in cylindrical NMR sample cells machined from sapphire, Lucalox, or beryllia bonded onto Nb with a nickel-titanium brazing alloy and closed with Nb-Nb cone seals. The concentrations are uncertain because of weighing errors by about 0.1% in the atomic fraction x $(\mathrm{Cs}_x\mathrm{Au}_{1-x})$, or about 0.3% in the excess metal concentration y $[\mathrm{Cs}_y(\mathrm{CsAu})_{1-y}]$, for small values of y. For samples close to stoichiometric CsAu the relative degree of stoichiometry was monitored by the spin-lattice relaxation rate at room temperature after formation of the compound. This rate has been shown[13] to be extremely sensitive to small amounts of Cs in solid CsAu.

The ^{133}Cs NMR was observed by standard coherent pulsed NMR techniques using frequencies in the range 9–13 MHz. Resonance shifts were measured relative to an aqueous CsCl solution, corrected to infinite dilution.[14]

Our experimental results for the ^{133}Cs resonance shift and relaxation rate are shown in Fig. 1. The shift is always paramagnetic and decreases slowly with increasing Au content over a wide range from pure Cs. However, for excess Cs concentrations below 20% the shift drops much more rapidly and below about 7% excess Cs, the shift *linearly* approaches a minimum value for stoichiometric CsAu. For the sample closest to stoichiometry, the observed shift is 750 ± 20 ppm at 600 °C. On the Au-rich side, the shift is nearly independent of concentration and only slightly larger than for CsAu.

The spin-lattice relaxation rate $1/T_1$ varies slowly over most of the range Cs–CsAu but at about 7% excess Cs it increases strikingly to a sharp peak of $1.2 \times 10^{+4}$ s^{-1} before falling rapidly as stoichiometry is approached. For CsAu and Au-rich alloys the concentration-independent rate

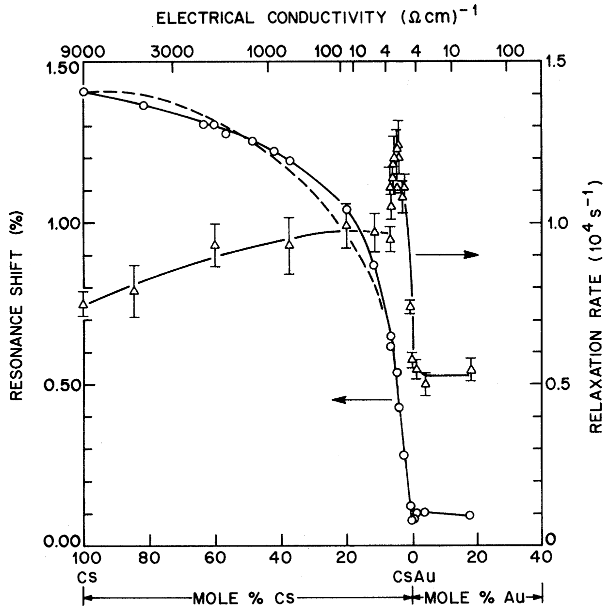

FIG. 1. ^{133}Cs resonance shifts (circles), defined according to the convention of the Knight shift, and nuclear relaxation rates (triangles) vs composition in liquid Cs-Au alloys at 600°C. Broken curve shows variation of the free-electron Pauli volume susceptibility normalized to the shift data for pure Cs. Upper scale shows the variation of the dc electrical conductivity (Ref. 2).

is still relatively high, being about $\frac{2}{3}$ that of pure Cs.

The variation of the shift over most of the range Cs-CsAu can be almost completely explained with use of the simple free-electron gas model. The Knight shift in a metal is given by

$$\Delta H/H \equiv K = (8\pi/3)\langle|\psi(0)|^2\rangle_F \Omega \chi_v^p , \qquad (1)$$

where χ_v^p is the Pauli volume susceptibility, and $\langle|\psi(0)|^2\rangle_F$ is the average electronic probability amplitude at the nucleus, normalized in a volume Ω. The concentration dependence of χ_v^p was calculated for a free-electron gas under the assumption of a density of one electron per excess Cs atom[15] and can be seen in Fig. 1 to provide a good representation of the gross features of the data. Deviations from the variation of the free-electron susceptibility can be attributed to variations in $\langle|\psi(0)|^2\rangle_F\Omega$, mainly due to perturbation of the charge density in the electron gas associated with the Au$^-$ ions, and to changes in the electron exchange-correlation enhancement of χ_v^p which were not included.

The NMR results demonstrate that the itinerant-electron system characteristic of Cs-rich alloys abruptly becomes unstable with respect to formation of localized states when the electron/atom ratio falls below about 0.07. Observation of large shifts, up to half that of pure Cs, when the dc conductivity is $\lesssim 10$ $(\Omega\ \mathrm{cm})^{-1}$, together with the *linear* variation of shift with concentration strongly implies localization below about 7% excess Cs.[16] Much more direct evidence for localization is provided by the peak in the relaxation rate as can be seen from the approximate (but very general) expression

$$1/T_1 \cong n\langle(A/\hbar)^2\rangle\tau , \qquad (2)$$

where n is the number of unpaired electrons responsible for the nuclear relaxation, $\langle(A/\hbar)^2\rangle$ is the mean square value for the hyperfine coupling, and τ is the correlation time characterizing fluctuations of the local hyperfine field. Since the smooth variation of the shift precludes drastic changes in either the number of electrons or the hyperfine coupling,[17] the observed rapid increase in $1/T_1$ can only be associated with a sharply increased correlation time, i.e., an increased lifetime for the hyperfine field produced by a particular electron.

An estimate of the variation of the hyperfine correlation time through the transition can be deduced from simple models of the itinerant- and localized-electron systems. In the itinerant range the relaxation rate can be expressed in the form[18]

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\mathrm{Korr}} \frac{\tau}{\hbar N(E_F)} , \qquad (3)$$

where $(1/T_1)_{\mathrm{Korr}}$ is the Korringa relaxation rate and $N(E_F)$ is the density of electronic states (per electron) at the Fermi level. The second factor in Eq. (3) is close to unity for "nearly-free-electron" metals in which the electron mean free path λ exceeds the average interatomic spacing a. For these metals, the Korringa rate adequately explains the observed relaxation, once electron-electron effects are properly taken into account. For strong scattering with $\lambda \sim a$, incipient localization lengthens τ and leads to enhancement of the rate relative to $(1/T_1)_{\mathrm{Korr}}$. This effect is clearly evident in Fig. 2 where we show the variation of τ calculated from Eq. (3) and free-electron values of $N(E_F)$.

In the localized range we first estimate the mean hyperfine coupling $\bar{A}$ by assuming a Curie-law susceptibility for the localized electrons.

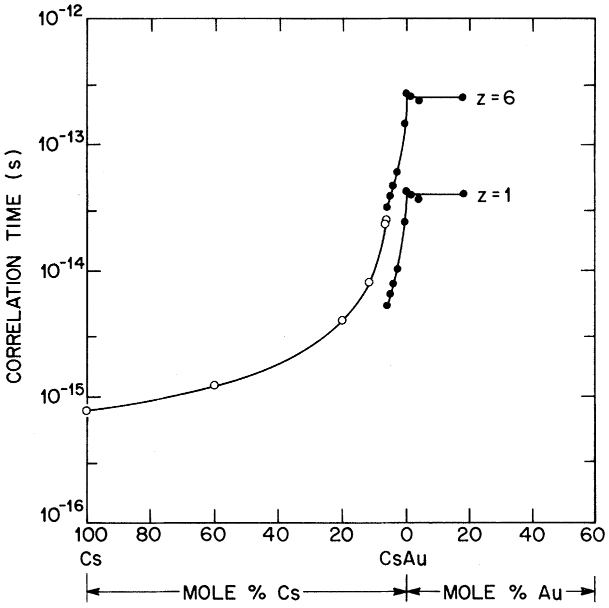

FIG. 2. ^{133}Cs hyperfine field correlation times vs composition in liquid Cs-Au alloys. Itinerant-electron values (open points) are calculated from Eq. (3). Values in the localized range (closed points) calculated from Eq. (5) for atomic states ($z = 1$) and F-center states ($z = 6$).

The shift is then

$$\frac{\Delta H}{H} = c\bar{A}\left(\frac{\gamma_e}{\gamma_n}\right)\frac{S(S+1)}{3k_BT}, \qquad (4)$$

where c is the concentration of localized electrons. Now the relatively high relaxation rate and residual shift observed for stoichiometric CsAu and Au-rich alloys indicate the presence of a small nearly composition-independent concentration c_0 of localized unpaired electrons. Extrapolation to 0 of the $1/T_1$ data near stoichiometry and of $\Delta H/H$ to the chemical shift of crystalline CsAu ($\Delta H/H = 360$ ppm)[19] leads to $c_0 = 0.004$. Thus, in the range Cs-CsAu, $c = c_0 + y$. The observed shifts for $y \leq 0.07$ and Eq. (4) yield $\bar{A} = 1.31 \pm 0.11$ GHz, or about 60% of the 6s atomic value. This result suggests that if the localized states are atomiclike, then the wave functions are considerably more extended than in the free atom so as to produce a 40% reduction in the probability amplitude at the nucleus. Alternatively, as suggested by Pitzer[20] for molten metal-halide solutions, the excess electrons might form a state like an F center with roughly equal amplitudes on z Cs$^+$ ions. For $z = 6$, such as is observed in neutron diffraction,[21] the field on a particular neighboring ^{133}Cs nucleus would be 10% of the free-atom value. This is a typical magnitude for the first neighbor hyperfine field around F centers in alkali halide crystals.[22]

The relaxation rate for localized paramagnetic centers is given by

$$1/T_1 = (2/3)S(S+1)c\langle (A/\hbar)^2\rangle\tau, \qquad (5)$$

where $\langle A^2\rangle = z^{-1}\bar{A}^2$. Values of τ obtained from the experimental rates and Eq. (5) are shown in Fig. 2 for $z = 1$ (atomic states) and $z = 6$ (F centers). Values of τ in stoichiometric CsAu are roughly two orders of magnitude longer than for pure Cs. As the excess Cs concentration is increased, τ rapidly becomes shorter and, for $z = 6$, joins the values obtained with the itinerant model with little discontinuity. The assumption of atomic states leads to an unrealistic discontinuity in τ since there is no large discontinuity in $1/T_1$.

We suggest that the background concentration c_0 of unpaired electrons results from thermal electron-hole pair generation: $\mathrm{Cs}^+ + \mathrm{Au}^- \to \mathrm{Cs}^0 + \mathrm{Au}^0$, where Cs^0 and Au^0 denote, respectively, electrons and holes, which could be localized in vacancies and Au$_2^-$ ions as F and V centers, respectively. The observed temperature dependence of $\Delta H/H$ and $1/T_1$ implies an activation energy in the range 0.2–0.3 eV for this process. It is noteworthy that no evidence of delocalization occurs at the Cs nuclei in the Au-rich mixtures, even for excess metal concentrations approximately 3 times greater than that for delocalization in the Cs rich mixtures.

In summary, we have measured the resonance shift and nuclear relaxation rate through the metal-nonmetal transition in Cs-Au alloys. There is clear evidence for abrupt formation of localized states close to stoichiometry. Hyperfine coupling strengths and correlation times suggest that these states are most likely to be analogous to F centers.

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Observation of a Strongly Enhanced Magnetic Susceptibility of Pd in Au-Pd-Au Sandwiches

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Exceptionally large increases in the magnetic susceptibility (indicating nearly magnetic ordering) of thin films of Pd sandwiched between thicker Au films have been observed at low temperatures—presumably due to the expansion of the Pd average lattice constant by the Au. The large resultant Stoner factors and the modified paramagnon model of Levin and Valls indicate the possibility of observing p-wave superconductivity in Pd structures with reduced proximity effects.

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Magnetism has been sought in Pd metal since the first recognition of its "incipient ferromagnetic" nature and the large effects of spin fluctuations.[1,2] With its high density of states at the Fermi energy and large Stoner exchange enhancement ($S \simeq 10$), it is easily polarized by dilute magnetic impurities leading to giant magnetic moments, and often to ferromagnetism at relatively high temperatures. More recently, interest in p-wave superconductivity has focused on Pd as a most likely candidate[3,4] because it has the largest value of S for pure metals; however, experimental studies[5] with very pure samples yield no superconductivity down to 1.7 mK. The observation of superconductivity[6] in irradiated Pd at $T_c \leq 3.2$ K demonstrates that drastic changes in the electronic and magnetic properties of a metal with large S may be expected with changes in its structure, presumably in this case because the disorder suppresses the spin fluctuations.

It is well known that changes in the properties of materials are often caused by application of high pressures which decrease the lattice pa-