Spin Polarization in the High-H_{c_2} Compound $Sn_{0.5}Eu_{0.5}Mo_6S_8$

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NMR studies of ^{95}Mo show that the enhancement of H_{c_2} (~ 100 kG) in Eu-substituted $SnMo_6S_8$ arises from a negative s-band spin polarization at the Mo site. Mössbauer-effect studies of ^{151}Eu indicate a small positive polarization at the Eu site and a weak Korringa relaxation, which is consistent with the weak depression of T_c. The Eu^{2+} isomer shift (− 14.0 mm/sec) shows an extremely low s-electron density at the rare-earth site.

The high-critical-field Chevrel-phase superconductors have attracted a great deal of attention recently due to their unusual superconducting[1,2] and phonon[3,4] properties. A particularly remarkable feature is that alloying paramagnetic rare-earth ions into the compounds can enhance the critical field H_{c_2} without substantially altering the superconducting transition temperature. For example, Fischer and co-workers[1] report that in the compounds $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$ one obtains $H_{c_2}(2\text{ K}) \approx 400$ kG and $T_c = 10.2$ K for $x = 0.5$, while $H_{c_2} \approx 275$ kG and $T_c = 10.4$ K for $x = 0.0$. They suggest that the result is related to the Jaccarino-Peter mechanism,[5] in which exchange coupling of the conduction electrons to the localized moment results in a negative conduction-electron polarization. This in turn produces a negative exchange field in the material which partially compensates the externally applied field. While such phenomena may often be present, the enhancement of H_{c_2} is not usually seen since a decrease in T_c (and hence H_{c_2}) due to exchange scattering from the localized moment usually predominates. However, in the Chevrel-phase compounds, the dependence of T_c on the magnetic-impurity concentration shows that exchange scattering is weak, and therefore, a net enhancement of H_{c_2} may occur. We report here the first *direct* measurements of the conduction-electron spin polarization in $Sn_{0.5}Eu_{0.5}Mo_6S_8$, by means of the ^{95}Mo nuclear magnetic resonance (NMR), the ^{151}Eu Mössbauer effect, and bulk magnetization measurements.

The samples for the NMR measurements were made with 96% isotopically enriched ^{95}Mo in order to suppress the resonance from the naturally abundant ^{97}Mo, which has a nuclear electric-quadrupole moment Q about 9 times larger than ^{95}Mo.[6] The NMR measurements were made with a phase-coherent high-power pulsed spectrometer operating at 13 MHz. The magnetic field was supplied by a superconducting solenoid. Field-sweep data were accumulated in a boxcar integrator and real-time data were accumulated in a Biomation digitizer (8-bit, 0.5-μsec), Nicolet signal averager (1024 channels). For the $Sn_{0.5}Eu_{0.5}Mo_6S_8$, the ^{95}Mo NMR field sweeps at 77 K yield spectra for the central transition ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) that indicate a second-order nuclear electric-quadrupole interaction with $3e^2qQ/[2I(2I-1)h] = 1.3$ MHz, asymmetry parameter $\eta \approx 0$, and axial Knight shift $K_{ax} \simeq 0$. There is essentially no inhomogeneous magnetic broadening (no magnetic echo); and the isotropic Knight shift is $K_{iso} = +0.63\%$ relative to $\gamma/2\pi = 2.774 \times 10^2$ Hz/G. At lower temperatures, the spectra are inhomogeneously broadened by a distribution of Knight shifts. (The low-temperature spectra were obtained by field sweeps while the magnetic echo was integrated by a boxcar.)

Mössbauer-effect spectra, at various temperatures and as a function of externally applied field at 4.2 K, were obtained using a source of 400-mCi ^{151}Sm in a Sm_2O_3 matrix. For the measurements in applied field, both source and absorber were kept in the field. This causes only a minor broadening of the source linewidth. Zero-field spectra showed a prominent single line with an isomer shift of -14.0 ± 0.1 mm/sec corresponding to Eu^{2+}, and a minor second line indicating Eu^{3+} in a quantity of ~ 5% of the Eu content.

For $T > T_c$, magnetization measurements were

made using the Faraday method in a superconducting solenoid. The samples studied in the investigation were powdered samples made by procedures similar to those published previously.[7] The transition temperatures, measured by a mutual-inductance technique and a calibrated Ge thermometer, are $T_c = 13.3$ K for $SnMo_6S_8$ and $T_c = 13.0$ K for $Sn_{0.5}Eu_{0.5}Mo_6S_8$.

Magnetization measurements and Knight-shift measurements have been obtained both in $SnMo_6S_8$ and in $Sn_{0.5}Eu_{0.5}Mo_6S_8$. The susceptibility of $SnMo_6S_8$ increases only by 8×10^{-6} emu/Mo between 77 and 20 K, and hence is essentially temperature independent. In this same compound, the isotropic Knight shift is $K_{iso} = +1.55\%$, also independent of temperature in the normal state. Below T_c, there is a change $\Delta K_{iso} = +0.4\%$. This change is due to a superconducting gap which opens at the Fermi level and leads to a quenching of the predominantly d-like Pauli paramagnetism. Since the core polarization field is negative,[6] a negative term in the Knight shift is quenched.

As shown in Fig. 1, the results for $Sn_{0.5}Eu_{0.5}Mo_6S_8$ are very different. The magnetization σ follows a Brillouin function $B_{7/2}(x)$, appropriate to Eu^{2+}, with a saturation value slightly less than that for the free-ion value. This smaller saturation value is partially due to the nonmagnetic Eu^{3+} in the material, but may also reflect a net negative conduction-electron polarization. The Knight shift shows a very large temperature dependence in the normal state. On passing through T_c ($x \cong 1$ in the figure), there is a change $\Delta K_{iso} = +0.38\%$, which is similar to that found in the pure $SnMo_6S_8$ and presumably arises from the same source. However, much of the large negative shift is not quenched at T_c. This appears to be a case of two-band superconductivity; i.e., at T_c a gap opens in the d band, but the s band is unaffected.[9] In Fig. 2, we have plotted K_{iso} vs σ. For $T > T_c$, one finds $K_{iso} = [1.265 - 6.95\sigma(NgS\times\mu_B)^{-1}]\%$. This proportionality between K_{iso} and σ suggests that the Knight shift arises from a negative conduction-electron polarization at the Mo site due to a rare-earth–conduction-electron coupling of the form $-2J_{sf}\,\overline{S}_{4f}\cdot\overline{s}_{5s}$. We assume,

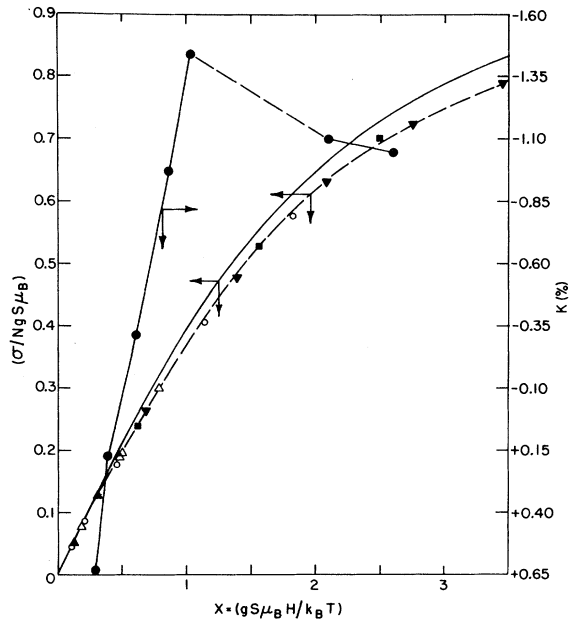

FIG. 1. Reduced magnetization ($\sigma/NgS\mu_B$) and ^{95}Mo Knight shift K as a function of $x = gS\mu_B H/k_B T$ for $Sn_{0.5}Eu_{0.5}Mo_6S_8$. Normal-state magnetization (dashed curve) obtained at 13.6 K (▽), 15.1 K (□), 20.5 K (○), 48.6 K (△), and 75 K (△). Solid curve for $\sigma/NgS\mu_B$ is the Brillouin function $B_{7/2}(x)$. Knight-shift data for $x > 1.5$ was obtained in the superconducting state. The values of H are the applied field corrected for the demagnetizing field (Ref. 8). Absolute shift can be obtained by multiplying 46 863 G by $K/(1+K)$.

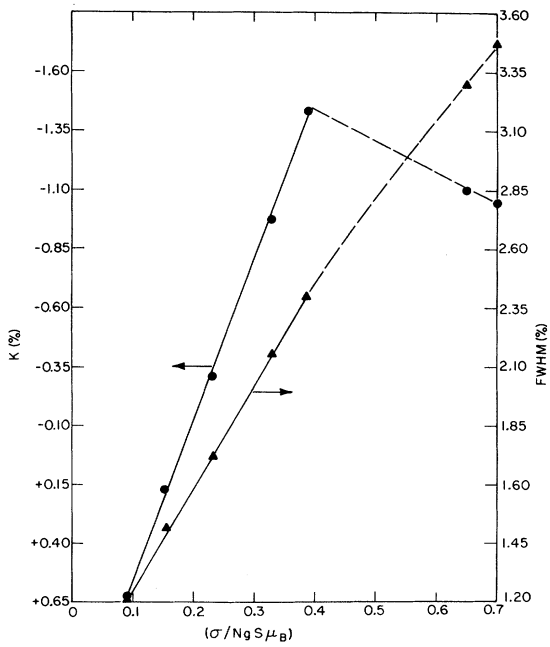

FIG. 2. Knight shift K and full width at half-maximum (FWHM) linewidth of ^{95}Mo as a function of reduced magnetization ($\sigma/NgS\mu_B$). NMR data in superconducting state indicated by dashed lines. Absolute shift and linewidth can be obtained by multiplying 46 863 G by $K/(1+K)$ and the FWHM by $1/(1+K)$, respectively.

based on the ^{95}Mo and ^{151}Eu linewidth results, very weak coupling to the Mo-derived 4*d* states. The linewidth of the ^{95}Mo resonance is shown as a function of reduced magnetization in Fig. 2. The proportionality to σ indicates a distribution of Knight shifts probably due to different Eu^{2+} environments about the ^{95}Mo, i.e., random replacements of Sn by Eu^{2+}. Since there is only a small change in slope of the linewidth versus σ in the superconducting state, it is clear that the coupling of the conduction electrons to the Eu^{2+} in the superconducting state is essentially unchanged from that in the normal state, i.e., *s*-band coupling to Eu^{2+}.

The ^{151}Eu Mössbauer effect has been measured in $Sn_{0.5}Eu_{0.5}Mo_6S_8$. Values of the hyperfine field H_{hf}^{Eu} at 4.2 K have been obtained in external fields of 15 and 60 kG. When extrapolated to saturation using a $B_{7/2}$ Brillouin function, both measurements give a hyperfine field of -285 ± 15 kG. Fully polarized Eu^{2+} ions in insulators show a saturation hyperfine field due to core polarization of -340 kG.[10] Therefore, we have a contribution due to conduction-electron polarization of $\sim +55$ kG. If this contribution is due to a contact interaction from polarized *s* conduction electrons,[11] then the conduction-electron polarization at the Eu site is positive. In other Eu intermetallics, the conduction-electron contribution to the hyperfine field varies from +40 to +200 kG.[11] The value obtained here, at the lower extreme of these values, indicates a rather small value of the *s*-state conduction-electron spin polarization at the Eu site.

A low total *s*-electron density at the Eu is strongly indicated by the observed isomer shift of -14.0 mm/sec. Such a shift is typically obtained for Eu^{2+} in ionic compounds, and is anomalous for conducting systems. In Eu^{2+} intermetallics, isomer shifts of about half this value are more common.[12] In addition, an indication of a small conduction-electron density of states at the Fermi level at Eu is shown by the strongly temperature-dependent Eu linewidth that is roughly proportional to $1/T$ in both $Sn_{0.5}Eu_{0.5}Mo_6S_8$ and $Sn_{0.75}Eu_{0.25}Mo_6S_8$. The linewidth dependence on temperature undoubtedly arises from Korringa relaxation of the Eu magnetic moments due to exchange scattering of the conduction electrons, i.e., the spin relaxation rate of the Eu magnetic moment $T_1^{-1}\sim[J_{sf}N(0)]^2T$. In other dilute Eu systems, Korringa relaxation is not observed because the larger values of $J_{sf}N(0)$ give a relaxation time that is too short (the fast relaxation regime $\omega_{hf}T_1\ll 1$, where ω_{hf} is the Larmor frequency of the ^{151}Eu nuclear moment in H_{hf}^{Eu}) to be effective in broadening the Eu linewidth.[13]

We may summarize the above results within the context of a simplified view of these complex materials. We consider the system to contain two bands which we label the "*s* band" and the "*d* band." The superconducting properties are dependent on the *d* band, presumably derived largely from the Mo ions.[2] Below the superconducting transition temperature, a gap opens in the *d* band causing the observed change in the Knight shift. When paramagnetic ions are added to the material, a rather weak exchange interaction occurs, largely with the *s* band. Also, a shielding of the Mo *d* electrons from the Eu site, which is surrounded by sulfur atoms, inhibits exchange scattering of the *d* electrons off the Eu^{2+} moments, and so T_c is weakly dependent on the magnetic-ion concentration. Therefore, the primary effect of the magnetic ions is to cause a polarization of the *s*-band electrons when the Eu^{2+} moments are aligned in an external field. This polarization is parallel to the field at the Eu site, but shows a spatial dependence such that it is negative at the Mo site. Below T_c, no gap opens in the *s* band so this polarization remains. As a result, there is a partial compensation of the applied field at the Mo sites due to weak *s*-*d* exchange coupling, inhibiting pair breaking of the *d*-band electrons and causing an enhancement of the critical field over that in the pure $SnMo_6S_8$.

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Influence of a One-Dimensional Superlattice on a Two-Dimensional Electron Gas*†

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We report unusual structure in the dc conductivity below 4.2 K as well as nonperiodic oscillations in the magnetoconductance of a two-dimensional electron gas in Si at low magnetic fields. A model of a superlattice with a gap which varies with carrier density is proposed to interpret the results. The superlattice appears to be of a somewhat general nature although the cause is not yet known.

The recent interest in quasi two-dimensional systems[1] and artificial superlattices[2] stems in a large part from the fact that one may essentially build new physical systems. In the former case one can reversibly change the carrier density or Fermi energy, while in the latter the Brillouin zone and the band structure are modified.

We have studied Si metal-oxide-semiconductor field-effect transistors (MOSFET's) which exhibit behavior different from that usually observed. These observations can be explained within the framework of a model of a superlattice structure at the Si-SiO_x interface. We expect this behavior to occur in general in a certain class of MOSFET systems. These results, therefore, illustrate the approach that many textbooks take in explaining lattice effects and Fermi surfaces.[3]

The consequences of a one-dimensional superlattice can be most easily seen by considering an isotropic two-dimensional electron gas (2D EG) in the presence of a one-dimensional potential with a first Fourier component of

$$V_x = V_1[\exp(2\pi ix/a) + \exp(-2\pi ix/a)].$$

This potential will mix states with k vectors differing by the reciprocal lattice vector $2\pi/a$. For k near π/a, first-order degenerate perturbation theory gives energies $\epsilon = \epsilon_x + \epsilon_y$ with $\epsilon_y = \hbar^2 k_y^2/2m$ and

$$\epsilon_x = (\hbar^2/2m)(k_x - \pi/a)^2 + \epsilon_0\{1 \pm [(4\hbar^2/2m\epsilon_0)(k_x - \pi/a)^2 + \alpha^2]^{1/2}\},$$

where $\epsilon_0 = (\hbar^2/2m)(\pi/a)^2$, and $\alpha = V_1/\epsilon_0$. At $k_x = \pi/a$, we have $\epsilon_x = \epsilon_0(1 \pm \alpha)$, i.e., there is an energy gap of $2V_1$ at the zone boundary.

Some properties of this system will be a strong function of Fermi energy (i.e., n_s). For small values of α and low n_s and also for very large n_s the behavior should be similar to that for the usual 2D EG. As the Fermi energy approaches the top of the first band, the density of states becomes very large and then decreases when the Fermi energy is in the gap. There is a discontinuous increase in the density of states when the Fermi energy enters the second band.

Because of the behavior of the density of states, we expect a w-shaped structure in the conductivity. The conductivity decreases near the band edges because of the increase in scattering caused by the increase in the density of states. In the y direction the conductivity with ϵ_F in the gap should increase with increasing n_s as the scattering is