In previous work on W(100), analogous behavior has been found. Waclawski and Plummer measured the intensity of the surface-state emission as a function of photon energy from 7.7 to 21.2 eV.[3] Their graph of surface-state emission intensity per incident photon versus photon energy extrapolates to zero at ~23 eV. This would be expected within the present interpretation. As the photon energy exceeds the bulk plasma energy, the contribution of the $\vec{p}\cdot\vec{A}$ term to the photoemission falls approximately to zero.

All these observations are consistent with the peak at 0.5 eV being produced by the $\vec{p}\cdot\vec{A}$ mode of ionization. Theoretical calculations[6,7] indicate that the surface state extends approximately three atomic layers into the surface while the $\vec{p}\cdot\vec{A}$ term is effective in ionization only to a much smaller depth (~1 Å). Although the peak at 0.5 eV may arise from ionization of the surface state within the first surface layer, one would expect that in the absence of the $\vec{p}\cdot\vec{A}$ effect ($h\nu > 23$ eV) emission from the surface state would still be produced by the dipole mechanism. For example, the peaks induced by the adsorption of oxygen and hydrogen are not very sensitive to photon energy, suggesting that these are photoionized mainly by the dipole mechanism. The conclusion to be drawn from this is that the surface state does not behave in the manner expected for such a species.

A possible explanation for the peak at 0.5 eV is that there exist wave functions at the surface (such as the 6s orbitals of tungsten extending into the vacuum beyond the 5d orbitals) which contribute only a small fraction to the total density of states. These could receive significant enhancement in photoemission intensity by the $\vec{p}\cdot\vec{A}$ term and not be observed when only the $\vec{A}\cdot\vec{p}$ term operates.

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Muon-Spin Depolarization in Spin-Glasses

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Polarized μ^+ particles were stopped in spin-glass alloys CuMn and AuFe. A sharp onset of the relaxation of the muon's polarization was observed in the vicinity of the transition temperature and is interpreted as arising from the dipolar fields of frozen impurity moments. Increased temperature width of the transition in an applied magnetic field is observed as a broadening of the internal-field distribution, extending through the transition.

We have used measurements of the spin precession of polarized positive muons implanted in the spin-glass alloys CuMn and AuFe to observe the static, local magnetic-field distribution associated with magnetic ordering. The technique has been used previously to measure local fields in a number of materials.[1] In studies of this type the muons can be considered as radioactive protons occupying random interstitial sites in the alloy. Muon spin precession as observed via oscillations in the emitted positron intensity ($\mu^+ \rightarrow e^+ + \nu + \bar{\nu}$, $\tau = 2.2$ μsec), at a fixed angle, is a sensitive measure of the local magnetic field. Previous techniques used to measure internal fields in spin-glasses include Mössbauer effect[2] and nuclear and electron-spin resonance.[3]

Confirmation a few years ago[4] of the existence of a sharp phase transition in the magnetic susceptibility of alloys of a few percent concentration of magnetic impurities, first observed in the Mössbauer-effect hyperfine field, led to renewed theoretical interest[5,6] in these unique materials. It is believed that below a certain freezing temperature, the magnetic impurities, which interact via the oscillatory long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect exchange, order into configurations which are neither ferromagnetic nor antiferromagnetic. The term glass is used to connote the absence of long-range spatial spin order.

Among the first theoretical treatments of local-moment interactions[7-10] were the random-molecular-field theories in which the fields experienced by individual spins are expected to be broadly distributed, as magnetic ordering sets in at low temperatures. In its original formulation, theory did not predict a phase transition.[10] Adkins and Rivier[5] developed a modification allowing for a short-range–order phase transition. However, the most recent theoretical proposals[6] show that short-range order in itself is not necessary for a spin-glass transition. There is a finite expectation that a spin S_1 will freeze below the ordering temperature T_c in the absence of short-range order. A mean-field order parameter q, defined as an average of S_i^2 over the system for a long time span, behaves like $1 - T/T_c$ near T_c.[6] One could expect $\sqrt{q}$ to correspond to mean polarization of the individual spins which in turn dictates the breadth of the internal field distribution.

In the muon precession experiment, as in a Cu NMR experiment, the Larmor precession frequency is influenced by both the direct magnetic dipolar fields from the magnetic impurities and the contact fields from conduction electrons polarized by RKKY interactions. RKKY fields are weaker by the factor $J_{sd}/2E_F$, 0.1 for copper,[11] where J_{sd} is the exchange energy at zero wavevector[12] and E_F the Fermi energy. The situation is analogous to the static inhomogeneous line broadening seen in host NMR.[11] However, for muons, the relative strengths of the two sources of internal field are reversed, as Cu host nuclei experience additional large hyperfine fields due to core electrons. Using NMR terminology, the muon depolarization time, T_2^*, is equivalent to an effective linewidth defined by $\Delta = (\gamma_\mu T_2^*)^{-1}$, where $\gamma = 8.51 \times 10^4$/G sec.

Samples for these experiments were prepared by quenching the melt and cold rolling, followed by an anneal and a second quench. Two specimens, $CuMn_{0.7\%}$, of 40 cm^2 area by 1 cm thickness, and $AuFe_{1.5\%}$, 30 cm^2 area by 1 cm thickness, were studied in detail. Ordering temperatures of 7.7 and 11.6 K, respectively, were determined by low-field ac susceptibility measurements on several small pieces cut from each sample: Variations of several tenths of a degree in the position of the susceptibility cusp were noted. The cryostat used had a thickness of 0.48 g/cm^2 of aluminum, and the plastic detectors defining the muon beam were 1.6 mm thick. The experiments were performed at the Space Radiation Effects Laboratory synchrocyclotron. The magnetic field was applied transverse to the muon's initial polarization (and beam) direction.

In a local field of arbitrary direction, the muon's spin precesses in a cone coaxial with the local field. After a brief residence time the decay positron is emitted preferentially along the muon's spin, and the positron detection rate is proportional to the cosine of the angle between the spin and the detector direction. Positron detectors were positioned at 0° and 90° relative to the beam, and data were simultaneously collected with 0.5- and 4-nsec/channel resolutions using time-to-amplitude converters and 2048-channel analog-to-digital converters. The muon stopping rate was 7×10^3 sec^{-1}. Raw data of positron counts as a function of time show asymmetry oscillations characteristic of the muon's precession frequencies. When a small constant background (about 15%) and the radioactive-decay exponential factor are removed, we obtain asymmetry factors as a function of time, such as are shown in Fig. 1 for the 0° detector, for $CuMn_{0.7\%}$ at two temperatures straddling T_c. Damping of the signal is due to dephasing in an inhomogeneous field, referred to as "slow" depolarization.

Nonlinear least-squares fits to the data were made, in which the precession frequency, asymmetry decay (T_2^*), asymmetry amplitude, and phase were fitted parameters. Typical fits for an exponential decay are also shown in Fig. 1. Reduced χ^2's averaged 1.2; fits to a Gaussian depolarization produced values about 5% higher. The χ^2 ratio of 1.05 has a 20% chance of being random. We therefore chose to use the exponential time for T_2^*.

Most of the data were taken by cooling in the measuring field, such as the example of Fig. 1. Values of Δ obtained from fits to data collected

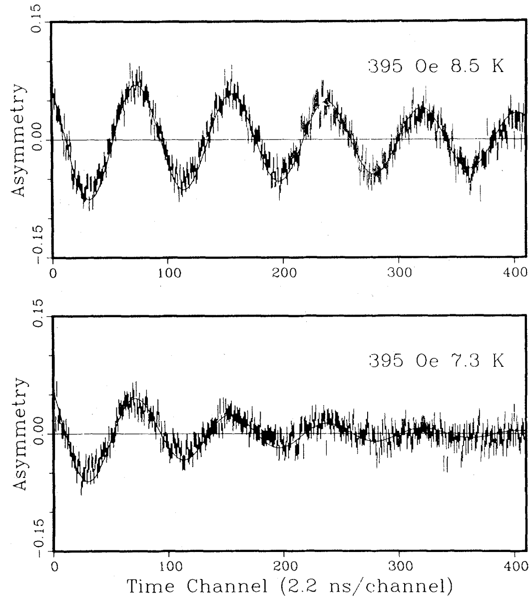

FIG. 1. The asymmetry in the positron detection signal versus the muon's residence time in the $CuMn_{0.7\%}$ sample; $T_c = 7.7$ K. Error bars denote the standard statistical error of the data. The sample was field-cooled from 20 K to the measuring temperatures indicated. The solid line is the nonlinear least-squares fit to the data for exponential decay.

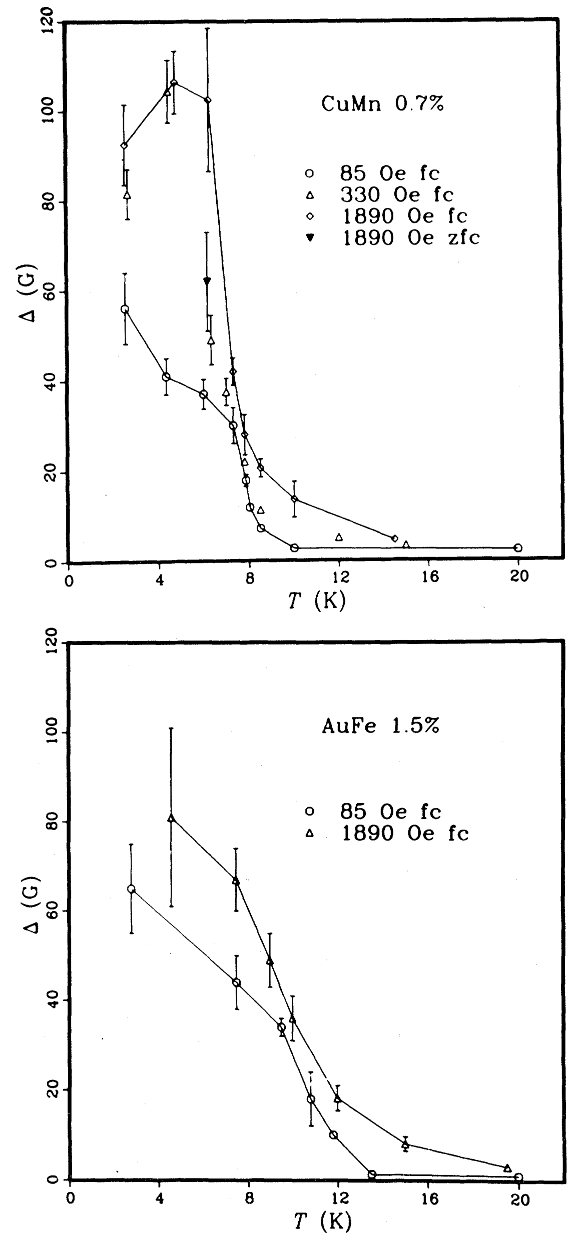

FIG. 2. Depolarization rate, expressed as a linewidth in gauss, plotted against sample temperature for several values of the applied magnetic field. T_c is 7.7 K for CuMn and 11.6 K for AuFe. fc corresponds to field cooling, zfc to zero-field cooling (one point in the CuMn data is shown). Error bars are combined statistical standard error and standard error of the mean of several measurements. The solid lines connect points taken under similar conditions.

by the two positron detectors were combined, and are shown as a function of temperature and applied field in Fig. 2 for the two specimens. To within an experimental uncertainty of about 10 G there were no shifts in the precession frequencies at low temperatures. This is to be expected, since the magnetization in the fields applied here is small.[13]

Additional experiments explored the magnetic remanence effect[13,14] by cooling in a strong (2500 Oe) field and taking precession data in a weaker (275 Oe) field. Specimens of $CuMn_{1.5\%}$, $CuMn_{3.0\%}$, $CuFe_{1.5\%}$, and $AuFe_{1.5\%}$ were surveyed. A large Δ was observed for all data taken below the T_c's, and a small Δ above. Furthermore, when the measuring field was reduced to zero, no precession oscillations were observed. (A Fourier-transform spectrum was studied in each case.) In the absence of an external field, an isotropic internal-field distribution of unique magnitude would result in oscillations of reduced amplitude in the 0° detector data.

Linewidth calculations for the NMR case have been made by Walstedt and Walker for the fields of dipolar and RKKY sources.[15] From application of their results for a random frozen spin configuration, the dipolar and RKKY contributions to the muon linewidth in $CuMn_{0.7\%}$, considered separately, are found to be 84 and 6.4 G, respectively. The calculated dipolar line shape is very close to a Lorentzian. For $AuFe_{1.5\%}$ the calculated dipolar linewidth is 71 G. These estimates should be insensitive to the details of the ordering in the spin-glass phase,[16] and should scale with the average value of the local moment. These estimates agree fairly well with the low-temperature limiting values of the measured Δ's.

We have drawn the following conclusions from our data:

(a) At the ordering temperature, there is a rather abrupt appearance of local fields that cause muon depolarization. The steep slope for Δ near T_c at low fields suggests agreement with the mean-field theory of freezing.[6] (There is a background contribution to Δ from nuclear dipolar fields, which in Cu is on the order of 1 G.[17])

The data taken in weak fields do not show a gradual onset of local ordering, predicted by the random-molecular-field theories.[10] A small amount of local ordering would lead to appreciable dipolar broadening in Δ above T_c. However, fluctuations on the time scale of local-moment precession frequencies would be averaged out in our experiments.

(b) The smearing of the transition in an applied field is due to the creation of larger local fields, both above and below T_c. Apparently, this is why resonance experiments done in a strong field fail to see a sharp transition point.[3] Field cooling produces stronger fields than zero-field cooling; see Fig. 2. We associate previous observations of a field effect on the magnetic susceptibility[4] and on the remanent magnetization[13,14] with induced spin freezing.

(c) The results are consistent with a random selection of interstitial sites by the muons.

(d) The local-field distribution contains no strong peaks or singularities. Such an effect might be expected for a static conduction-electron spin-density wave, a picture proposed by Overhauser in an early theory on this subject.[9]

The apparent observation of a well-defined Mössbauer hyperfine field has been attributed to a saturation effect,[18] and therefore does not contradict the muon and NMR observations of a broad internal field. The data do not support the existence of a finite probability density of zero molecular field, such as proposed by Marshall[8] and by Klein and Brout[10]. If a substantial fraction of the magnetic impurities experience weak fields, in turn producing weak dipolar fields, the observed linewidths would be much smaller.

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Dynamic Low-Spin–High-Spin Transition of Fe^{2+} in $1T$-$Fe_xTa_{1-x}S_2$ ($x \leq \frac{1}{3}$)

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$1T$-$Fe_xTa_{1-x}S_2$ shows unusual behavior in the temperature dependence of the magnetic susceptibility and ^{57}Fe Mössbauer isomer shift, as a result of a low spin ($^1A_{1g}$) to high spin ($^5T_{2g}$) transition of Fe^{2+}. The fluctuation rate $^1A_{1g} \leftrightarrow {}^5T_{2g}$ is faster than 10^7 sec^{-1}.

A number of studies of pure metallic layered compounds and their substitutional or intercalated alloys have centered on the recently discovered charge-density-wave (CDW) instability.[1] Here we report the magnetic susceptibility (χ) and ^{57}Fe Mössbauer effect in $1T$-$Fe_xTa_{1-x}S_2$, which shows unusual magnetic behavior completely unlike any of the pure,[1] substituted,[1] or intercalated[2] layered compounds. We show that this is due to a dynamic low-spin–high-spin transition of Fe^{2+} with increasing temperature.

$1T$-$Fe_xTa_{1-x}S_2$ has the CdI_2 structure[3,4] (neglecting small distortions due to the CDW) which is the stable structure to at least 800°C when $x \geq 0.02$. X-ray and electron diffraction studies indicate that the Fe is randomly (or almost so) distributed on Ta sites; no evidence of Fe ordering is seen at any $x \leq \frac{1}{3}$. 200-kV transmission electron diffraction studies clearly show the existence of a CDW in these compounds at room temperature for $x \leq 0.10$; at $0.15 \leq x \leq \frac{1}{3}$ diffuse scattering is seen, but no sharp satellite peaks are seen that would indicate a CDW with a long coherence.[5] It is possible that in the latter range of x the CDW is not the ground state of the system, but that local distortions[6] or even short-range Fe order account for the diffuse scattering. The presence of CDW may affect the low-spin–high-spin transition, but its effects are not quantitatively known. We return to this point later.

The magnetic susceptibility per mole of Fe (χ_m) is shown in Fig. 1 for powder samples at different x.[7] The data clearly show that Fe has no magnetic moment at low temperatures, but that at high temperatures a moment appears, which for low x approaches the Curie χ_m expected for Fe^{2+} in the high-spin state ($S = 2$, $g = 2$). At high temperatures there is a change in behavior when $x \geq 0.15$, in that χ_m approaches the same value independent of x. Only at $x = \frac{1}{3}$ were small thermal hysteresis effects observed (as shown).

One would expect that the valence of Fe in a sulfide would at most be 3+, the only other possibility being 2+. Since the Fe is in approximate octahedral coordination, there are only four possible magnetic states: Fe^{2+}, $S = 0$ (low spin), $S = 2$ (high spin); Fe^{3+}, $S = \frac{1}{2}$ (low spin), $S = \frac{5}{2}$ (high spin). Clearly the magnetic data show that Fe^{2+}, $S = 0$, occurs at low temperatures, but the high-temperature data could be consistent with a change to high-spin Fe^{2+} or high-spin Fe^{3+}.

We have examined the nature of the iron spin state by using the ^{57}Fe Mössbauer effect in $Fe_xTa_{1-x}S_2$ (for $x = 0.10$ and 0.33). A character-

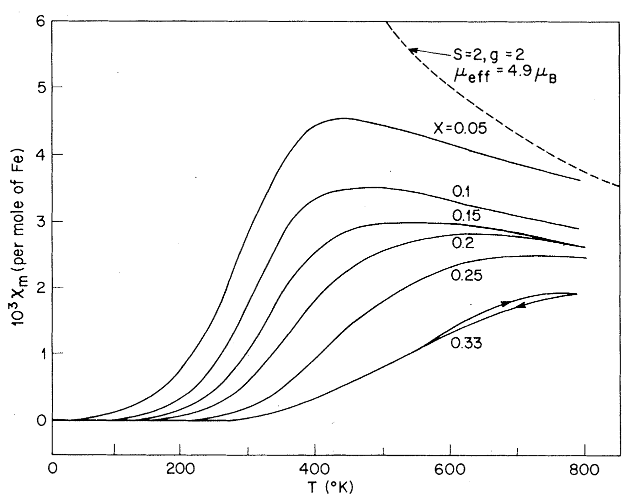

FIG. 1. Magnetic susceptibility per mole of Fe (χ_m) for $1T$-$Fe_xTa_{1-x}S_2$ powder ($0.05 \leq x \leq \frac{1}{3}$) versus temperature.