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Nuclear-magnetic-resonance study of electronic structure in the copper-niobium superlattice

M. Yudkowsky and W. P. Halperin
Department of Physics and Materials Research Center, Northwestern University, Evanston, Illinois 60201

Ivan K. Schuller
Materials Science and Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

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Cu nuclear-magnetic-resonance studies of a Cu/Nb superlattice reveal that the Cu in the superlattice is divided into at least two electronically distinct regions. One region has a small anisotropic Knight shift and a spin-lattice relaxation rate approximately 30% larger than ordinary Cu. The other region has large dipolar isotropic and anisotropic frequency shifts; its spin-lattice relaxation rate is up to two orders of magnitude smaller than that of ordinary Cu.

Artificially constructed composition modulations in binary metallic films have been used to investigate atomic diffusion,[1] superconductivity,[2] magnetism,[3] and structural[4] and elastic[5] properties. The films are made by coevaporation of two metallic elements to produce a periodic compositional variation along the growth direction. Structural information such as the wavelength of the composition profile and its amplitude can be inferred from x-ray measurements with the help of phenomenological models.[6]

There are two distinct classes of metallic superlattices. In one, the constituent elements, usually of the same crystal structure, naturally form a continuous set of solid solutions; in this case, the composition variation introduced during fabrication is inherently unstable. Examples of these are Cu/Ni and Ag/Pd. In the other class the elements are not mutually soluble, leading to very little intermingling of the constituents except possibly at the atomic planes directly adjacent to the interfaces. Schuller[6] first reported the synthesis of this letter type of film with the elements copper (fcc) and niobium (bcc). X-ray,[6] optical,[7] electrical,[8] and superconducting[9] measurements have been carried out on this material. As yet, however, there is very little information about the electronic structure, where it might be expected that the periodic interruption of the lattice potential would play an important role. We present here copper nuclear-magnetic-resonance (NMR) measurements on a Cu/Nb sample which show that there are indeed significant differences in the local electronic environment as seen by Cu/Nb nuclei as compared with that seen by ordinary metallic Cu nuclei. These effects are particularly evident in NMR satellite resonances that we associate with the presence of the Cu/Nb interface. These resonances exhibit large anisotropic and isotropic frequency shifts, and exceedingly small spin-lattice relaxation rates (T_1^{-1}).

The Cu/Nb superlattices used in this experiment were produced by alternately sputtering equal thicknesses of Cu and Nb. A detailed description of the apparatus and procedure is presented elsewhere.[6] The thickness of each pair of Cu and Nb layers, called a wavelength, was 5.75 ± 0.25 nm, meaning that there were, on the average, 13.8 atomic planes in each Cu layer. The total thickness of each superlattice was 7.69 ± 0.38 μm. The substrates were sapphire, 0.5 by 0.5 by 0.003 in. Seventeen samples were made at one time and studied simultaneously.

The pulsed NMR spectrometer used in this experiment is an improved version of one described by Gibson *et al.*[10] Measurements were made of spectra and the spin-lattice relaxation times T_1 at a resonance frequency of 10.8 MHz, at temperatures of 77, 4.2, and 1.7 K, and a number of magnetic fields. Observations were made of both isotopes of copper as a function of the angle θ between the magnetic field and the growth direction of the superlattices (the copper [111] direction and the niobium [110] direction). To obtain our spectra, a phase alternating (PAPS) sequence of $\pi/2$ pulses was used with varying repetition rates. After sorting according to phase the free induction decays were averaged together, fast Fourier transformed, and converted to polar coordinates, yielding a magnitude and phase spectrum. Although sensitivity was not uniform over the displayed bandwidth, this was independently calibrated. The magnetic susceptibility was measured using a SHE Corporation VTS-10 variable temperature susceptometer.

The magnitude spectrum shown in Fig. 1 indicates the unusual character of Cu/Nb. The spectrum is taken in the vicinity of the resonance of metallic ^{65}Cu and it clearly shows a resonance at the expected position, 0.1212 MHz/T. We shall refer to this resonance as the "bulk-Cu" resonance. The other resonances seen at approximately 2% lower frequencies are unexpected. We shall refer to these resonances as the "shifted-Cu" resonances. A copper reference sample was prepared by sputtering Cu alone onto a mica substrate. By comparison with this reference, we

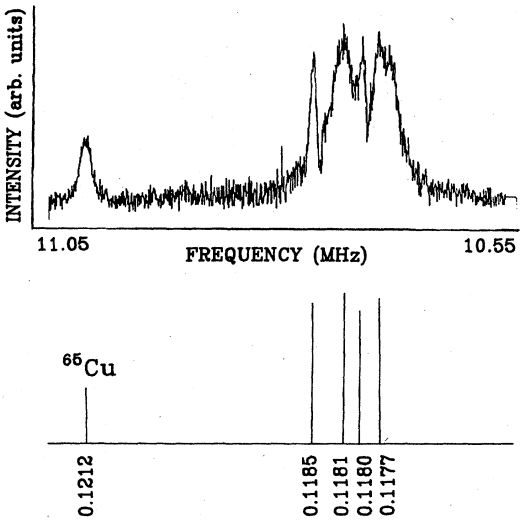

FIG. 1. Typical magnitude spectrum of Cu/Nb, taken at 1.7 K and at $\theta = -8°$. The spectrum shows ^{65}Cu; it is centered at 10.8 MHz and is 0.5 MHz wide. The numbers across the bottom are the frequencies divided by the field, in units of MHz/T, and serve to identify the lines.

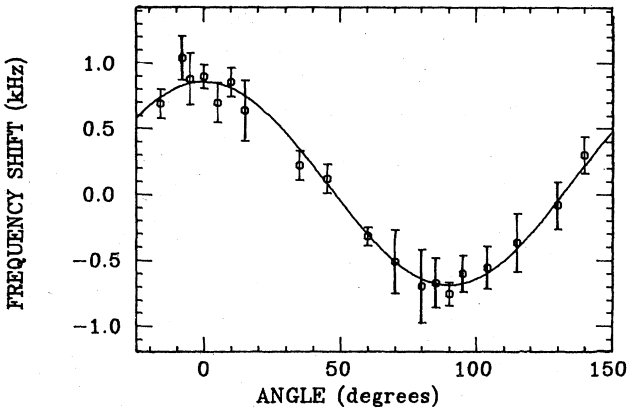

FIG. 2. Frequency shift of Cu/Nb relative to a reference sample of copper powder as a function of angle, corrected for the dimagnetization effect. These ^{63}Cu data were taken at 4.2 K. The fit is to the equation $\Delta f = a_0 + a_2 \cos^2\theta$.

have found that 19% of the copper nuclei in the Cu/Nb superlattice appear in the bulk-Cu resonance and 63% of the copper nuclei appear in the shifted-Cu resonances. The latter includes another smaller group of resonances appearing at still lower frequencies, not shown in Fig. 1; in addition, the accuracy of the data for shifted Cu suffered because of the plethora of lines which appeared in the system. The remainder of the copper nuclei were not detected. This interpretation of the spectrum amplitudes presumes that the resonances we observe correspond to all magnetic transitions for copper nuclei: $-\frac{3}{2} \leftrightarrow -\frac{1}{2}$, $-\frac{1}{2} \leftrightarrow \frac{1}{2}$, and $\frac{1}{2} \leftrightarrow \frac{3}{2}$. This point will be discussed below.

The bulk-Cu resonance frequency was studied in detail as a function of angle. Comparisons were made with a reference sample of copper powder, prepared by filing a 99.999% pure copper bar; the powder was contained in a cylindrical tube with axis parallel to the NMR coil. The angular dependence found for the bulk-^{63}Cu resonance frequency is shown in Fig. 2. These shifts are corrected for the demagnetization effect[11] using measured values[12] of the susceptibility of Cu/Nb.

For a noncubic, axially symmetric metal, the anisotropic Knight shift K_a may be expressed as

$$\Delta\omega/\omega_0 = K_i + K_a(3\cos^2\theta - 1) \ , \tag{1}$$

where $\Delta\omega$ is the difference in frequency between the metal and a diamagnetic reference compound[12] resonating at frequency ω_0, K_i the isotropic shift, and θ the angle between the axis of symmetry and the external magnetic field. In our Cu/Nb samples, the axis of symmetry in the copper layers is the growth direction, the [111] direction of Cu. Fitting the data of Fig. 2, we find that bulk ^{63}Cu has an isotropic Knight shift of $0.230\% \pm 0.002\%$ and a small anisotropic shift K_a of $0.0048\% \pm 0.0003\%$. Similar results were obtained at other temperatures and for bulk ^{65}Cu. In ordinary copper, the isotropic shift is 0.239%, and—as for all cubic metals—there is no anisotropic Knight shift.[12] The linewidth in bulk ^{65}Cu was 10% wider than the reference and independent of angle.

These results are not consistent with an interpretation based on the nuclear electric quadrupole interaction; the constant linewidth implies that first-order satellites are not present, and the $\cos^2\theta$ dependence implies that the angular variation is not due to the second-order quadrupolar interaction. It appears, therefore, that the small changes in the isotropic Knight shift and existence of an anisotropic Knight shift have a magnetic origin. Either an anisotropic spin density coupled to the nucleus by the Fermi contact interaction or the electron-nuclear dipole interaction may be responsible. The latter can be nonzero where there is a deviation from cubic symmetry such as in the thin films investigated here.

Measurements of the spin-lattice relaxation times of bulk Cu as a function of temperature indicates that a Korringa mechanism is responsible where $T_1T = 0.83 \pm 0.15$ sK for ^{63}Cu and $T_1T = 0.68 \pm 0.30$ sK for ^{65}Cu, both measurements taken at 4.2 K (at 1.7 K, $T_1T = 0.65 \pm 0.03$ sK for ^{65}Cu). The reference Cu had T_1T's of 1.16 ± 0.06 sK and 1.11 ± 0.20 sK, respectively (at 4.2 K). Quadrupolar contributions to T_1 are not expected; using the known gyromagnetic ratios of the two isotopes, it was possible to confirm that quadrupolar contributions to T_1 were negligible.[13] The relaxation of the nuclear magnetization was found to be exponential over a wide range of times.[14]

The spin-lattice relaxation rate may be written as

$$1/T_1T = \sum_i F(i)[\gamma_e\gamma_n P_F(i)\rho(i)]^2 \ , \tag{2}$$

where γ_e and γ_n are the gyromagnetic ratios of the electron and the nucleus, respectively. $F(i)$, $P_F(i)$, and $\rho(i)$ are, respectively, constant factors, hyperfine fields, and the density of electronic states for different electron-nucleus interactions i: s-, d-, and d-band core polarization, orbital, etc.[15] A decrease in T_1T suggests either a higher density of states at the Fermi surface or more intense hyperfine fields. A higher density of states at the Fermi surface of the Cu is consistent with the expansion observed in the perpendicular lattice spacing using x-ray scattering.[16] The experimentally observed expansion has been speculated to be due to elec-

tron transfer from the Nb to the Cu layers, and gave rise to the elastic constant anomalies.[7]

In studying the shifted-Cu resonance it was immediately apparent that the resonance was not similar to that of any known cubic metal. We have observed large isotropic and anisotropic shifts as well as very long spin-lattice relaxation times, more characteristic of an insulator than a metal. Identification of the shifted-Cu resonances shown in Fig. 1 to the isotope ^{65}Cu followed only after a comparison of ^{65}Cu and ^{63}Cu NMR, plus careful analysis of the sample holder and substrate NMR spectra (which exhibit a strong quadrupolar split, angularly independent ^{27}Al spectrum).

At least five distinct regions in the spectrum can be associated with shifted Cu. Four of these are evident in Fig. 1; another region is at lower frequencies. The positions of the resonances varied as a function of angle; they were examined over the interval $-16° \leq \theta \leq 32°$, beyond which they overlapped the ^{27}Al and ^{63}Cu resonances. Nonetheless, this range was sufficient to identify a clear angular dependence for these resonances, such as given by Eq. (1) and shown by the solid curve in Fig. 3. The measured isotropic and anisotropic shifts for the 0.1185 line were 8.1% and 3.1%, respectively; the results were similar for the other shifted-Cu lines.

We now turn to the question of the origin of these frequency shifts and the importance of the quadrupolar interaction. For frequency shifts to first order in the quadrupolar interaction one would expect symmetry in the spectrum about the angle 55°. This is not observed. In addition, the angular dependence of the $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition to second order in the quadrupolar interaction is different from what is measured. More importantly, such a splitting varies as the inverse of the external field, whereas we observe the opposite dependence as shown in the inset to Fig. 3. Ruling out the quadrupolar interaction leads us to believe that the frequency shifts of shifted Cu are magnetic in origin.

The T_1's of the shifted-Cu lines are one to two orders of magnitude longer than that of ordinary Cu. For the line 0.1181 MHz/T in Fig. 1, T_1 is 93 ± 10 s. Other lines, further from the bulk-Cu line, had shorter T_1's, ranging from 63 ± 9 s to an estimated 5.3 s.

In summary, it appears that the copper in Cu/Nb is divided into two physically distinct regions. One, a "bulk-Cu" region, contains enough nuclei to make up ~ 3 atomic planes in each Cu layer. This region exhibits a small anisotropic Knight shift and reduced T_1. We speculate that this region is situated at the center of each copper layer. The other region is the "shifted-Cu" region, comprising enough nuclei to account for ~ 8 atomic planes in each Cu layer. It appears to be sufficiently magnetic to produce large isotropic and anisotropic frequency shifts, and at the same time has a very low electronic density of states. We speculate that the shifted-Cu region is situated in the 4 atomic planes on each side of the bulk-Cu planes.

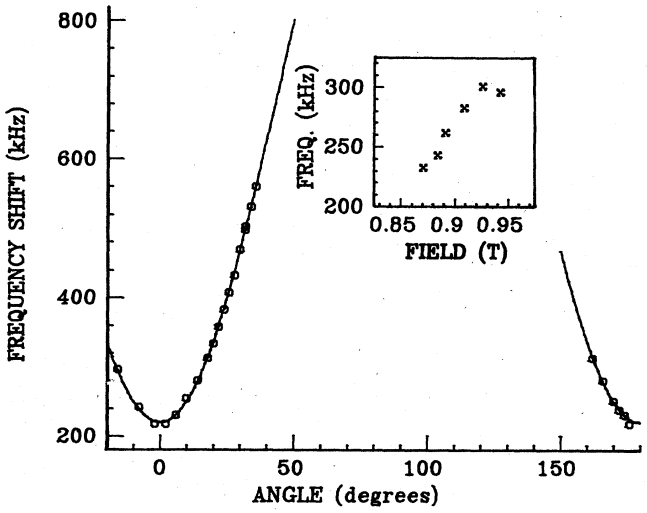

FIG. 3. Frequency shift (relative to bulk ^{65}Cu) of the 0.1185 MHz/T shifted-Cu line (Fig. 1) as a function of angle. The fit is to the equation $\Delta f = a_0 + a_2 \cos^2\theta$. Inset: The frequency shift, in kHz, of the 0.1185 MHz/T line increases with increasing magnetic field.

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