PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Growth and magnetic characterization of Mn films and superlattices on Ag(001)

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(Received 1 September 1988)

We have grown single-crystal Mn films and coherent (Mn/Ag) superlattices on Ag(001) and characterized the magnetic behavior with temperature-dependent ferromagnetic resonance and magnetic susceptibility measurements. We find that the Mn films exhibit a 2.89-Å square surface net identical to that of Ag(001), and a tetragonal structure similar to that of quenched γ-Mn. The (Mn/Ag) superlattices exhibit a well-defined high-angle x-ray-diffraction satellite structure. We detect no significant ferromagnetic contribution at temperatures down to 5 K, and conclude that the Mn is antiferromagnetically ordered.

A great deal of interest has recently focused on the properties of thin films and metastable phases of the magnetic 3*d* transition metals. The interplay between the lattice structure (particularly the atomic volume) and magnetic behavior has emerged as an especially fruitful area of study, as direct comparisons can now be made between the magnetic properties predicted by spin-resolved first-principles calculations and those measured experimentally.[1-3] Total-energy calculations have been shown to be particularly important in identifying ground-state properties and studying magnetic behavior as a function of volume.[3,4]

Recent calculations have investigated the low-temperature volume dependence of the magnetic behavior for bcc (Refs. 4–6) and fcc (Ref. 6) Mn, phases which occur naturally, but at temperatures well above reasonable magnetic ordering temperatures.[7,8] At reduced temperatures, both phases are predicted to order magnetically above some minimum lattice constant, with substantial values for the magnetic moment: bcc Mn is expected to exhibit a ferromagnetic ground state for $a_0 \geq 2.75$ Å,[4-6] while the fcc phase is expected to have an antiferromagnetic ground state for $a_0 \geq 3.85$ Å.[6]

Experimentally, one may attempt to stabilize normally high-temperature or metastable phases of a material at reduced temperatures by epitaxial growth on a suitable substrate, so that the surface net of the substrate provides a template for growth of the overlayer at the desired lattice constant,[2,9,10] Such a template provides only an in-plane constraint, however. The layer spacing out-of-plane along the growth, however, is determined by minimization of the total energy, and for ultrathin films ($\lesssim 25$ Å) is difficult to measure independently. In general, one should not expect this spacing to equal the in-plane spacing to yield a cubic structure.

Heinrich and co-workers have studied Mn overlayers on Ru(0001), Fe(001), and Ni(001) substrates in an effort to expand the Mn lattice to produce magnetic moments approaching the Hund's rule limit of $5\mu_B$.[9,11] They used reflection high-energy electron diffraction (RHEED) to determine the in-plane atom spacing, i.e., the surface net. While complex phases of Mn form on both Ru(0001) and Ni(001) substrates, growth on Fe(001) produces Mn layers with a surface net identical to that of the substrate for several monolayers (ML), from which the authors conclude that the Mn is bcc. Since growth on a bulk Fe substrate makes characterization of the Mn by conventional magnetic techniques very difficult, x-ray photoelectron core-level intensity measurements of the 3*s* satellite were used to infer that the Mn atoms spend a fraction of their time in a state with a magnetic moment of $5\mu_B$.[9,11] This technique does not measure magnetic order, however, and the interpretation of such data has been called into question and is not well understood.[12]

We have grown single-crystal Mn films and coherent (Mn/Ag) superlattices on Ag(001) and characterized the magnetic behavior with temperature-dependent ferromagnetic resonance (FMR) and magnetic susceptibility measurements. In a simple constant volume approximation based on the Wigner-Seitz radius of α-Mn (1.43 Å),[13] the stable phase at room temperature, one would expect a lattice constant of 2.89 Å for simple bcc Mn and 3.65 Å for fcc Mn. Total-energy calculations by Moruzzi and Marcus[4] predict equilibrium lattice constants of 2.79 and 3.51 Å for the low-temperature bcc and fcc phases, respectively, with the bcc lattice metastable with respect to the fcc.[14] The Ag(001) surface ($a_0 = 4.09$ Å) has a 2.89 Å square surface net, which coincidentally is nearly identical to that of Fe(001) upon a 45° rotation of the net about the surface normal.[15] Thus, one would expect the Ag(001) surface to serve as an excellent template with which to stabilize growth of bcc rather than fcc Mn at low temperature.

It is important to recognize, however, that the bcc and fcc structures are two special cases of the general tetragonal lattice—the fcc structure may be viewed as a continuous distortion of the bcc, and *vice versa*. Accordingly, total-energy calculations for these two cases should not be interpreted to predict the minimum-energy configuration for the material under study, as the large variety of tetragonal variations have not yet been examined for obvious practical reasons. In particular, assuming one could constrain the Mn lattice parameter in-plane via epitaxial growth to match that predicted for bcc Mn, there is no reason to expect a true bcc structure to result, as a tetragonal configuration may be the total-energy minimum for that choice of in-plane spacing. We find this to be the case for the epitaxial growth of Mn on Ag(001). From a combination of RHEED and x-ray photoelectron diffraction (XPD) data, we find that deposition of Mn on

the Ag(001) surface produces growth of a tetragonal phase which may be viewed as a distortion of either the simple bcc or fcc lattice along the surface normal.

The samples were grown in a PHI Model 400 molecular-beam epitaxy system equipped with Auger electron spectroscopy (AES) and RHEED. The Ag(001) substrate films were grown on 5 ML Fe(001) seed layers grown on ZnSe(001) epilayers, which were grown in turn on bulk GaAs(001) substrates. We have found these Ag films to be of superior quality to bulk single crystals, yielding x-ray double-crystal rocking curves of 300 arcsec for the (002) reflection, a factor of 2–6 smaller than that obtained from various preparations of bulk substrates.[16] The Mn films and (Mn/Ag) superlattices were deposited from independently shuttered Knudsen cell sources at substrate temperatures of −10 to 30 °C and Mn growth rates of 2–12 Å/min. The flux rates were monitored with a quadrupole mass spectrometer, and thicknesses were determined by x-ray fluorescence. The GaAs substrates were mounted with Ga to the sample holder, so that the samples were never heated above room temperature even when demounted. All samples were coated with a final 100-Å layer of Ag (followed in some cases by 100 Å of Al) to prevent degradation upon exposure to atmosphere. AES and RHEED were used to confirm surface cleanliness and determine the in-plane atom spacing during growth, respectively.

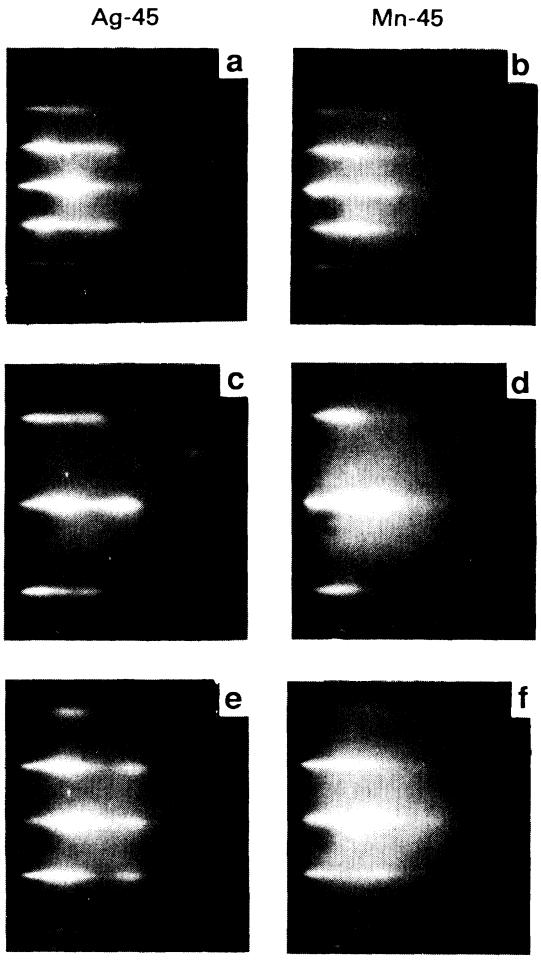

FIG. 1. RHEED patterns (10 keV) obtained from the 45th Ag and Mn layers in a 45-period superlattice consisting of 23-Å Mn and 44-Å Ag (001) layers. The electron beam is incident along the following azimuths, referred to the Ag(001) substrate axes: (a) and (b) [110], (c) and (d) [130], and (e) and (f) [010].

Figure 1 shows the RHEED patterns obtained from the 45th period of a (Mn/Ag) superlattice consisting of 23-Å Mn and 44-Å Ag layers for three in-plane azimuths. Note that the Mn and Ag patterns are the same for a given azimuth and exhibit a fourfold rotational symmetry, demonstrating that the Mn surface net is constrained to be identical to that of the Ag(001) surface. Note also that even after 45 periods of growth, the RHEED patterns exhibit well-defined streaks for both Mn and Ag layers, indicative of well-ordered single-crystal surfaces.[17] We find that growth of Mn much beyond 20–25 Å produces additional features in more poorly defined RHEED patterns, indicating either a surface reconstruction or more probably a transition to a different phase. The thickness at which this transition occurs increases with increased growth rates.

Figure 2 shows an x-ray θ-2θ scan around the Ag(002) reflection obtained from a 20-period (Mn/Ag) superlattice consisting of 8.6-Å Mn and 31-Å Ag layers. The central peak, which consists of overlapping contributions from the Ag base layer and the zeroth-order reflection from the layers in the superlattice itself, is flanked by five superlattice satellite peaks, cut off by the ZnSe/GaAs (002) reflection on the low-angle side and by an x-ray source impurity line on the high-angle side. This satellite structure is characteristic of coherent single-crystal superlattices,[18,19] and confirms the period and discrete layered nature of the sample.

X-ray photoelectron diffraction[20] results obtained independently[21] show that the Mn layers grow in a tetragonal phase rather than simple bcc or fcc. For thicknesses greater than or equal to 5 ML, the Mn films exhibit an XPD forward scattering peak along the [100] azimuth at

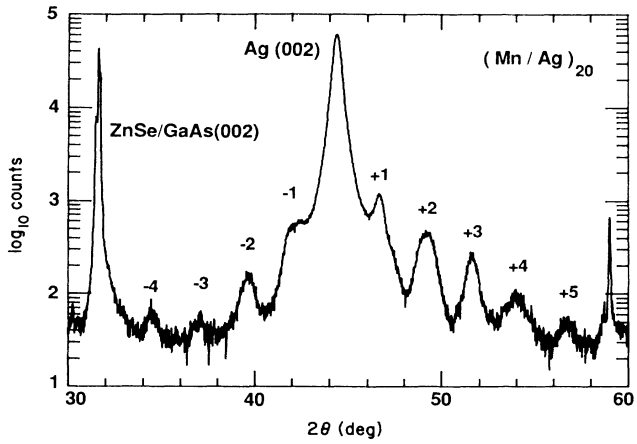

FIG. 2. X-ray θ-2θ scan (Cu Kα) around the Ag(002) reflection obtained from a 20-period (Mn/Ag) superlattice consisting of 8.6-Å Mn and 31-Å Ag layers.

polar angles approximately midway (51°) between the characteristic fcc (45°) and bcc (54.7°) peak positions. Given the 2.89-Å square surface net, this structure may be viewed as a tetragonally distorted version of either the fcc or bcc lattices, with a c/a ratio of 0.81 ($a=2.89\sqrt{2}=4.09$ Å, $c=3.31$ Å) or 1.15 ($a=2.89$ Å, $c=3.31$ Å), respectively. In either case the growth plane is (001). For film thicknesses less than 5 ML, the forward scattering peak shifts to lower angles (47°), but always appears above the 45° position characteristic of the fcc lattice. These results will be presented in greater detail elsewhere.[21] We restrict our attention here to films ≥ 5 ML thick. In addition, XPD shows that the growth is not ideal layer-by-layer at room temperature, with some population of the second Mn monolayer occurring before the first is completed.

The magnetic behavior of the Mn/Ag samples was studied using temperature-dependent FMR and magnetic susceptibility measurements. The superlattice samples had individual Mn layer thicknesses which ranged from 8.6 to 23 Å and up to 45 periods (see Fig. 1), so that one sample had a total of 1035 Å of Mn. The magnetic moment of a 5-mm-diam disk of each sample was measured over the magnetic field and temperature ranges of 0–40 kG and 10–300 K using a superconducting quantum interference device (SQUID) magnetometer, with the applied field in the plane of the sample. After correction for the diamagnetic contribution of the GaAs substrate, none of the samples studied showed a detectable ferromagnetic signal. Combining all sources of error, if the Mn is ferromagnetically ordered, we can put an upper limit of 17 G on the magnetization M at 10 K. This is only 1% of the low-temperature bulk Fe value of 1740 G.

These data also place an upper limit on the amount of intermixing which may occur at the Mn/Ag interface, as Mn atoms in Ag-rich Ag(Mn) alloys are known to exhibit large paramagnetic moments of $5\mu_B$ as determined thermodynamically.[9,11,22] If significant intermixing occurred, it would be especially evident in samples with the largest number of interfaces (periods). From a careful analysis of the field dependence of the magnetization obtained for the 45 period sample (assuming a Brillouin-type contribution with $J=\frac{5}{2}$ for the possible presence of paramagnetic Mn atoms), we conclude that less than 1.5% of the Mn atoms which make up the single Mn monolayer at each Mn/Ag interface diffuse into the Ag or participate in forming dilute Ag(Mn) alloys.

Each sample was also examined in FMR spectrometers at frequencies of 9.3 and 34.8 GHz at various temperatures down to 5 K. In no case could we detect an FMR signal which could be attributed to ferromagnetic Mn. Under essentially identical sensitivity conditions, a 12-Å single-crystal layer of Fe(001) grown on ZnSe (001) and overcoated with Ag gave a well-defined FMR signal with a linewidth W of 550 Oe. For a comparable linewidth, we estimate that any Mn FMR signal would have easily been detectable if it was 0.1 as intense as the Fe signal. Note that the total Mn thickness of 1035 Å in one sample then implies that the Mn magnetization, which is proportional to the signal intensity, is less than 0.12% that of Fe. The sensitivity of this technique falls off as W^{-2} if the linewidth of any Mn FMR signal were larger, but for lines up to 1500 Oe wide, one can say that the FMR data are consistent with the upper limit found in the SQUID magnetometer measurements.

These data show that even at low temperature, the Mn is not ordered ferromagnetically with a moment per atom above our detectability limit of $0.02\mu_B$. We conclude that in the tetragonal structure described, the Mn is either nonmagnetic or, more probably, ordered antiferromagnetically. Note that the tetragonal structure of Mn obtained by room-temperature epitaxial growth on Ag(001) as described here is quite similar to that of γ-Mn in its quenched state.[7,8] We find that the Mn films exhibit a 2.89 Å square surface net and a tetragonal structure which may be viewed as consisting of either body-centered tetragonal cells with $a=2.89$ Å, $c=3.31$ Å ($c/a=1.15$), or face-centered tetragonal cells with $a=2.89\sqrt{2}=4.09$ Å, $c=3.31$ Å ($c/a=0.81$). In either case the film surface is the (001) plane. The high-temperature (1100–1134 °C) fcc or γ phase of Mn, when quenched or alloyed with certain metals, also exhibits a tetragonal structure consisting of face-centered tetragonal cells ($a=3.77$ Å, $c=3.53$ Å, $c/a=0.94$),[7,8] or equivalently, of body-centered tetragonal cells ($a=3.77/\sqrt{2}=2.67$ Å, $c/a=1.32$).[23] Growth on the Ag(001) surface forces an in-plane expansion with a corresponding out-of-plane contraction relative to this quenched γ-Mn phase. Since quenched γ-Mn is a type-I antiferromagnet, we believe that the Mn films on Ag(001) are also antiferromagnetically ordered with the easy axis along [001].

We note that due to the similarity of the Ag(001) and Fe(001) surface nets,[15] growth of Mn on Fe(001) is also likely to produce the tetragonal structure described here rather than a bcc phase as reported elsewhere,[9,11] which was inferred only from the surface net. The out-of-plane spacing is an essential parameter in unambiguously deducing the lattice structure, although it is much more difficult to measure experimentally for ultrathin films. An antiferromagnetically ordered Mn film would also be consistent with the results of Heinrich, Arrott, Liu, and Purcell,[11] who found that overlayers of Mn on Fe(001) had no measurable effect on the Fe FMR lines.

A comparison with the magnetic behavior predicted for the low-temperature bcc and fcc phases[4–6] is not entirely appropriate due to the different lattice realized experimentally for Mn on Ag(001). It is interesting to note, however, that the effective Wigner-Seitz radius for the resultant tetragonal structure is 1.49 Å, in good agreement with the values exhibited by the various cubic or quenched phases of Mn (1.43–1.52 Å),[7,24] and significantly larger than the value of 1.37 Å obtained from the total-energy calculations of Moruzzi and Marcus.[4] As noted earlier, these calculations place a *cubic constraint* on the structure as dictated by the augmented-spherical-wave method used, and, therefore, do not consider tetragonal distortions which may lower the total energy. In the case of coherent epitaxial growth where the in-plane spacing of the overlayer is constrained to match the surface net of the substrate, tetragonal distortions ($c/a\neq 1$) or surface layer contractions along the surface normal are commonly observed. Hence, calculations most

relevant to the field of epitaxy should seek a minimum-energy configuration subject to a specified *in-plane constraint* (e.g., the surface net of a chosen substrate) by allowing the out-of-plane spacing to vary.

A calculation of this general nature was reported by Oguchi and Freeman,[25] who studied the tetragonal lattice distortion in bulk antiferromagnetic γ-Mn by calculating the total energy as a function of tetragonal distortion (c/a ratio) subject to a constant *volume* constraint rather than a surface net constraint. They obtain a calculated equilibrium ratio of $c/a=0.90$, somewhat smaller than the experimental value of 0.94,[7,8] and conclude that the distortion is due to a directional property of the d-band bonding resulting from the antiferromagnetic ordering. They generalize their results to predict that any strong antiferromagnet with uniaxial magnetic structure will distort via a contraction perpendicular to the ferromagnetic lattice plane,[25] as observed experimentally for γ-Mn.[7,8]

In conclusion, epitaxial growth of Mn on Ag(001) produces single-crystal films with a square surface net identical to that of the substrate, so that the in-plane atom spacing (2.89 Å) is within 4% of the lattice constant predicted by total-energy calculations for low-temperature ferromagnetic bcc Mn (2.79 Å).[4] We find, however, that the films exhibit a tetragonal rather than cubic structure, and conclude that the Mn is antiferromagnetically ordered, similar to quenched γ-Mn. Since tetragonal distortion or surface-layer contraction is commonplace in epitaxial systems and an additional complication in addressing magnetic ordering, we point out the need for calculations which assume an in-plane constraint on the atomic positions and allow the out-of-plane spacing to vary to obtain equilibrium.

The authors gratefully acknowledge helpful discussions with W. F. Egelhoff, K. B. Hathaway, and D. Papaconstantopolous, and thank W. F. Egelhoff for allowing us to cite his XPD results for Mn on Ag(001) prior to his own publication. We also acknowledge the technical assistance of D. King and F. Kovanic. This work was supported by the Office of Naval Research.

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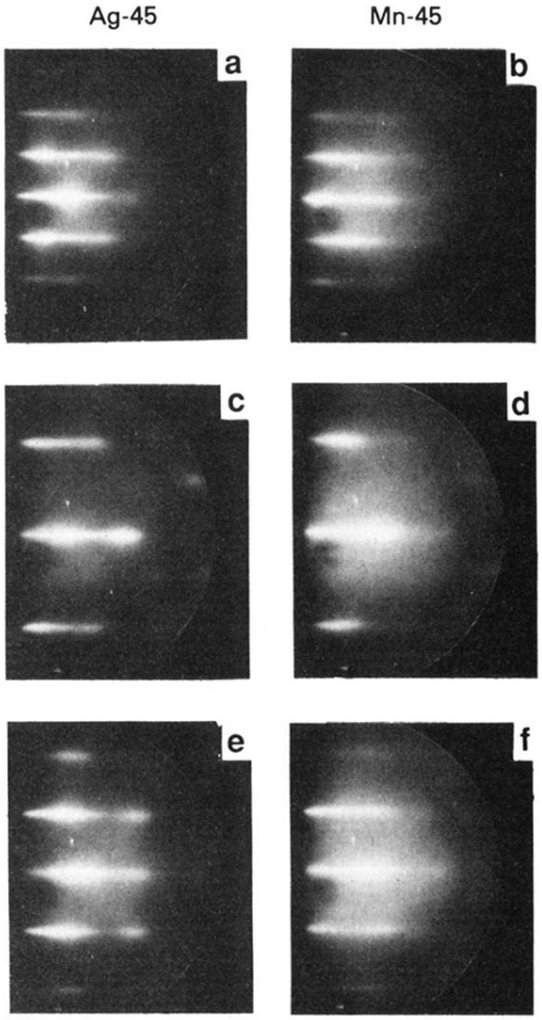

FIG. 1. RHEED patterns (10 keV) obtained from the 45th Ag and Mn layers in a 45-period superlattice consisting of 23-Å Mn and 44-Å Ag (001) layers. The electron beam is incident along the following azimuths, referred to the Ag(001) substrate axes: (a) and (b) [110], (c) and (d) [130], and (e) and (f) [010].