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Antiferromagnetic ordering in Co-Cu single-crystal superlattices

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Cobalt-copper single-crystal superlattices were grown by epitaxy on a Cu(100) substrate with different bilayer thicknesses between 20 and 30 Å. Polarized and unpolarized neutron-diffraction characterization shows good structural quality and antiferromagnetic ordering of the superlattices at zero field with the magnetic moments in the film plane. Magnetization measurements are consistent with the neutron data, showing a magnetic moment very close to the saturation value of bulk cobalt ($1.7\mu_B$) as well as a complex dependence on the applied magnetic field.

Layered magnetic systems with artificial periodicity have provided continuous scientific interest because of the various scale-dependent physical properties that they exhibit. In particular, remarkable magnetic properties of metallic superlattices have been reported in the past years.[1] The development of new preparation techniques has led to the production of crystalline superlattices of rare-earth elements, e.g., Gd/Y (Ref. 2) or Dy/Y (Ref. 3), with sapphire as a substrate. Thanks to their crystallinity many unexpected results have been found.[4,5] In particular, it has been shown that the coupling of ferromagnetic layers across nonmagnetic interlayers can become antiferromagnetic, e.g., Gd/Y (Ref. 4), helimagnetic, e.g., Dy/Y and Gd/Dy (Ref. 3), or can be more complex, e.g., Ho/Y (Ref. 5).

Less is known in the case of $3d$ magnetic transition metals, where the magnetic moments are smaller and where the electrons are itinerant, in contrast with the localized rare-earth systems. An early effort was devoted to the Cu/Ni system (Refs. 6 and 7) in which an epitaxial growth was expected. Unfortunately, the strong interdiffusion taking place at the interface produced a sine-wave chemical modulation rather than an ideal square-wave modulation.[8] In the case of $3d$ metals it is also of great interest to grow a single-crystal superlattice of X repeating bilayers, $(A_M/B_N)_X$, each bilayer consisting of M atomic planes of a magnetic metal A, and N atomic planes of a nonmagnetic material B.

The purpose of this paper is to report on the preparation and magnetic properties of single-crystalline superlattices of Co and Cu epitaxially grown on Cu(100) substrates. The multilayers were grown from the vapor phase and they exhibited long-range crystalline order as evidenced by unpolarized neutron-diffraction measurements. Also, polarized neutron-diffraction experiments reveal that the Co layers are antiferromagnetically ordered in the absence of any applied magnetic field. Furthermore, a magnetization measurements reveal a complex behavior as a function of the applied magnetic field. This will be briefly discussed in the following. The magnetic moment of the Co atoms calculated from the data of both experimental techniques indicate a value of $1.7\mu_B$ (close to the bulk value).

Cobalt atoms deposited on Cu(100) substrates kept at room temperature sit on the fourfold hollow sites and they form an ordered $p(1\times1)$ overlayer as evidenced by low-energy electron-diffraction spectroscopy (LEED).[9,10] Subsequent deposition results in a layer-by-layer type of growth as determined by Auger electron spectroscopy,[9,11] medium-energy electron diffraction (MEED) (Ref. 12), and thermal-energy atom scattering.[13] The last technique allows one to evaluate the quality of the growth,[14] determined by the efficiency of mass transport across the surface, i.e., by the surface diffusion coefficient. Deposition at room temperature results in an appreciable degrading of the surface flatness although the layer by layer sequential filling is maintained up to many layers. Deposition at elevated temperatures (500 K) would lead to an improved

surface ordering but it results in diffusion of Co to the bulk of the Cu substrate and, consequently, to mixed interfaces.[12,13]

The magnetic properties of (single) thin films of Co have been carefully characterized. The Co layers are ferromagnetically ordered below the Curie temperature (T_C). Upon increasing the layer thickness, T_C increases, reaching the (extrapolated) bulk value at 5 monolayers (ML).[12] The films are magnetized in plane and the hysteresis loops measured with surface magneto-optic Kerr effect (SMOKE) indicate single-domain behavior.[12] From a Co thickness of 5 ML on, the electronic structure of the film is in excellent agreement with the calculated band structure of bulk fcc Co, e.g., exchange splitting, band dispersion. . . , etc., as given by early angle-resolved[10] and recent spin-resolved photoemission.[13]

The Cu substrates utilized in the present work were cut from a single-crystal bar (1.3 cm^2) and oriented to within 0.3° of the ⟨001⟩ direction by Laue diffraction. After introduction in the UHV chamber they were cleaned *in situ* by cycles of sputtering with Ar^+ (600 eV, 1 $\mu A/cm^2$) and annealing to 1000 K. The surface cleanliness was checked with Auger electron spectroscopy (AES) and the average crystalline perfection of the substrate was characterized by means of thermal-energy atom scattering technique (TEAS). Prior to evaporation the surface consisted of flat terraces, 300 Å wide on average, separated by monoatomic steps.[13] The Co (Cu) layers were evaporated onto the substrate from carefully outgassed ovens heated by electron bombardment and equipped with mechanical shutters. The pressure in the chamber was in the 10^{-10}-Torr range during evaporation. A deposition rate much smaller (0.01 Å/sec) than those employed normally (≈ 6 Å/sec) was chosen in order to reduce surface imperfections. The thickness of the evaporated layers was determined by counting the number of oscillations in TEAS and cross checked with calibrated quartz balance. The samples were finally covered with 1000 Å of an epitaxial Cu buffer to protect the multilayer against exposure to air. It is known by depth-profiling analysis that oxygen does not penetrate more than 30 ML under these conditions.[15] In the following we will concentrate on data corresponding to two superlattices, namely $(6Co/8Cu)_{62}$ and $(9Co/5Cu)_{103}$, which display an almost identical periodicity and which were both grown at 300 K. Further details on the growth procedure and characterization will be given elsewhere.[13]

Neutron diffraction with the scattering plane perpendicular to the layer plane was used to verify the periodicity, the crystalline character, and the magnetic properties of the multilayer. The measurements were carried out on the triple-axis polarized neutron spectrometer IN20 at the Institut Laue Langevin (ILL) in Grenoble, France. A scheme of the experimental setup is displayed as an inset in Fig. 1, along with neutron-diffraction patterns for these two superlattices (SL). Both low- and high-Q satellites are observed in the data. The position of the satellites is related to the chemical modulation, Λ_{SL}, by $Q_m = m2\pi/\Lambda_{SL}$ (with $m = 1,2,3,\ldots$). From these data the periodicity of both superlattices $\Lambda_{SL} \approx 26.4$ and 26.6 Å, respectively, agrees to within 6% with bilayer thicknesses determined by TEAS and quartz balance.

The presence of the high-Q superlattice satellites located around (002) Bragg reflection of the Cu substrate illustrates the crystalline character of the multilayer. The small difference between the lattice parameter of the substrate and the average lattice spacing of the Co/Cu multilayer precludes the resolution of the main superlattice reflection from the very strong (002) substrate peak. The high-Q satellites have an asymmetrical shape which has been observed previously in multilayers[5,16] and is ascribed to (i) nonuniform d spacing, i.e., periodicity fluctuations, and (ii) lattice mismatch in the film. The relative intensity and position for the different satellites (in both superlattices) can be nicely reproduced by a simple step model calculation,[17] where the fluctuations in d spacing are of the order of the lattice mismatch (2%). On the other hand, the width of the high-Q satellites indicates coherence lengths of several hundred angstroms.

An additional observation in the data from Fig. 1 is the appearance of extra satellites with half-integer index $m = \frac{1}{2}, \frac{3}{2}, \ldots$ corresponding to a doubling of the chemical bilayer periodicity, $2\Lambda_{SL}$. A similar observation was reported for Gd/Y superlattices.[4] The extra satellites were assigned to antiferromagnetic ordering of the Gd layers. This assumption was verified by polarized neutrons and by the disappearance of the satellites with increasing temperature.[4]

To check the possible antiferromagnetic origin of these half-integer satellites we have used the available polarized neutron setup. The temperature was not raised, in this particular case, because interdiffusion could destroy the superlattice modulation. A monochromator-polarizer [Heusler (111)] and a flipper placed before the sample allows us to select neutrons of defined spin state (see Fig. 1 and Ref. 18 for details). A magnetic field in the range 1–10 kOe was applied parallel to the film plane and perpendicular to the scattering vector. In this configuration and without polarization analysis after the sample, the intensity measured in the flipper off condition (neutron spin antiparallel to the magnetic moments) is proportional to $(b+p)^2$, with b and p being, respectively, the atomic and magnetic scattering lengths. The intensity detected with flipper on (neutron spin parallel to the magnetic moments) is proportional to $(b-p)^2$.

The data corresponding to the $(6Co/8Cu)_{62}$ sample are shown in Fig. 2. The first obvious fact is that a field of 10 kOe, which saturates the magnetization of the sample at 10 K (see below), reduces the intensity of the half-integer satellite to zero. At smaller magnetic fields (1 kOe) the $m = \frac{1}{2}$ satellite partly appears indicating a partial antiferromagnetic or a more complex magnetic structure at small fields. The $m = \frac{1}{2}$ satellite has the same intensity in the flipper on and off configurations which indicates a purely magnetic origin (i.e., $b = 0$) for this satellite. The other possibility (i.e., $p = 0$) is not allowed because of the dependence on the applied magnetic field. On the contrary, the $m = 1$ peak almost vanishes in the flipper on condition (taking into account a finite flipping ratio) suggesting that b and p values are very similar, in agreement with the calculated value from the structural parameters of the superlattice. Actually, a quantitative analysis of

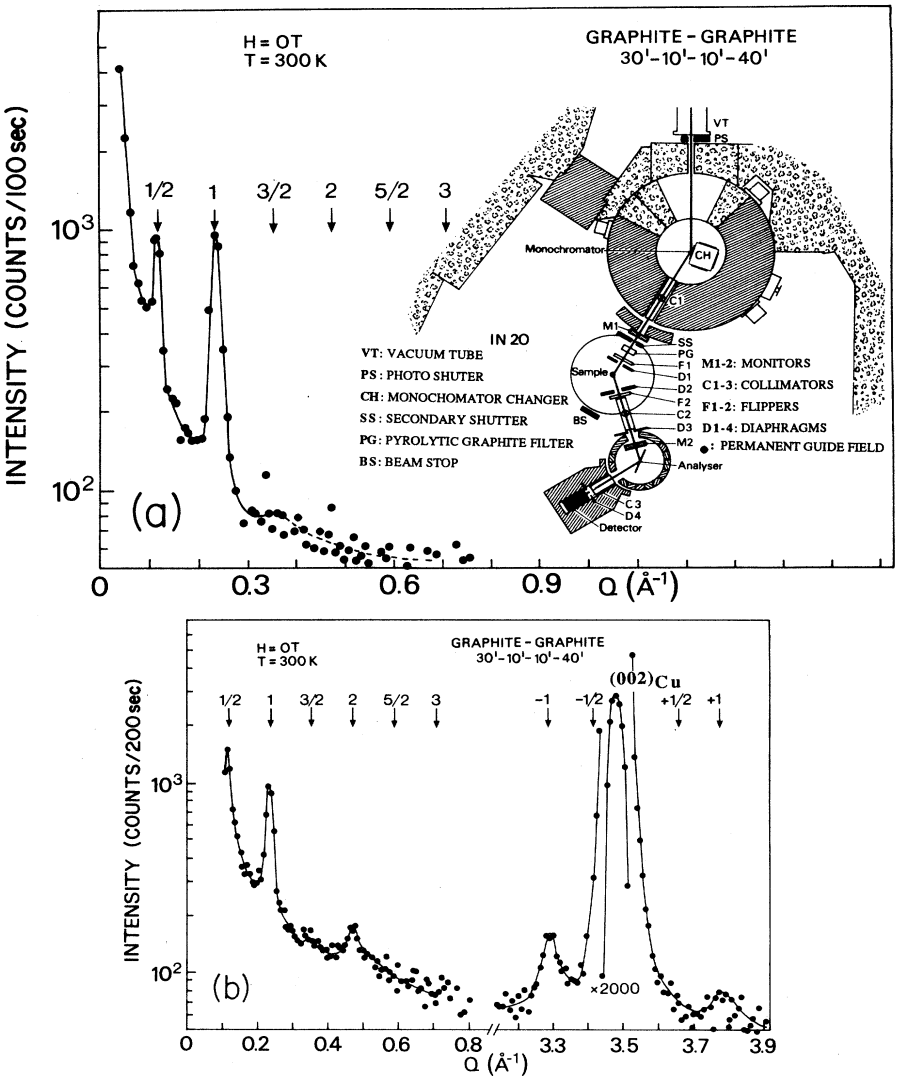

FIG. 1. Neutron-diffraction data for two different superlattices in the low- and high-Q regions, (a) $[6Co/8Cu]_{62}$ ($\Lambda_{SL}=26.4$ Å) and (b) $[9Co/5Cu]_{103}$ ($\Lambda_{SL}=26.6$ Å). The inset shows schematically the triple axis spectrometer used in the experiment with the polarized neutron setup. The lines are guides to the eye.

the ratio between flipper on and off intensities in our multilayer films allows one to estimate the magnetic moment of the Co atoms to be $1.7\pm0.1)\mu_B$, i.e., identical within the errors to the bulk fcc value, $1.71\mu_B$, as expected from previous spin-polarized neutron-reflection measurements.[19] The magnetic moment is confirmed to be in the layer plane as expected from SMOKE measurements.[12]

The magnetization of the multilayer films at varying temperatures was measured by means of a superconducting quantum interference (SQUID) magnetometer. Representative data taken at 4.2 K for low magnetic fields (≤ 1 kOe) applied parallel to the film plane of the $[6Co/8Cu]_{62}$ sample are shown in Fig. 3. The inset display the data for higher magnetic fields (until 40 kOe) showing that saturation was reached only around 8 kOe. The absence of superparamagnetic effects is consistent with the inexistence of isolated Co clusters and the picture of smooth surfaces. The value of the saturation magnetization leads to a Co moment of $(1.76\pm0.05)\mu_B$, very close to the bulk value ($1.71\mu_B$).

The hysteresis loop of Fig. 3 shows a complex behavior in the range of 0–0.5 kOe, indicating a reversion process of the magnetization from antiferromagnetic to ferromagnetic ordering. The temperature dependence of the saturation magnetization was measured up to 300 K (to avoid interdiffusion). It shows only a very small decrease (4%) suggesting that T_C is well above 300 K, probably close to the bulk Co value (1388 K).

Preliminary data (not shown here) taken with $H_{\parallel}$ at different directions in the plane reveal some degree of magnetic anisotropy in the plane. This in-plane anisotropy would be probably related to the difference between the ⟨100⟩ and ⟨110⟩ directions in the fcc structure of the Co layers.

Our findings can be rationalized as follows: At and below 300 K each group of 6 ML of Co is ferromagnetically ordered as shown by the polarized neutron data of Fig. 2 and spin-polarized photoemission spectroscopy

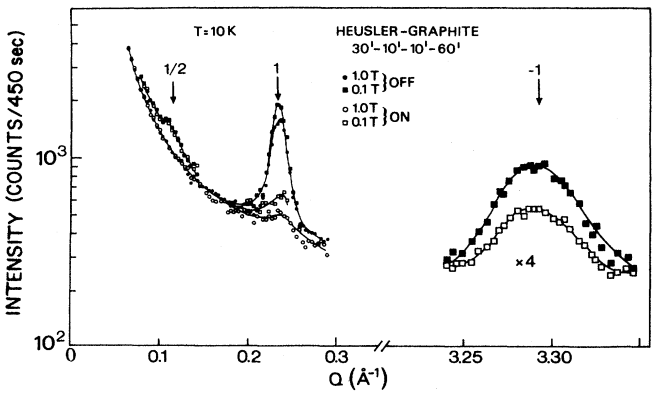

FIG. 2. Polarized neutron-diffraction scans in the low- and high-Q regions for two magnetic fields (0.1 and 1 T, i.e., 1 and 10 kOe, respectively) parallel to the layer. The magnetic satellite with index half-integer appears only for a magnetic field of 0.1 T (1 kOe). The lines are guides to the eye.

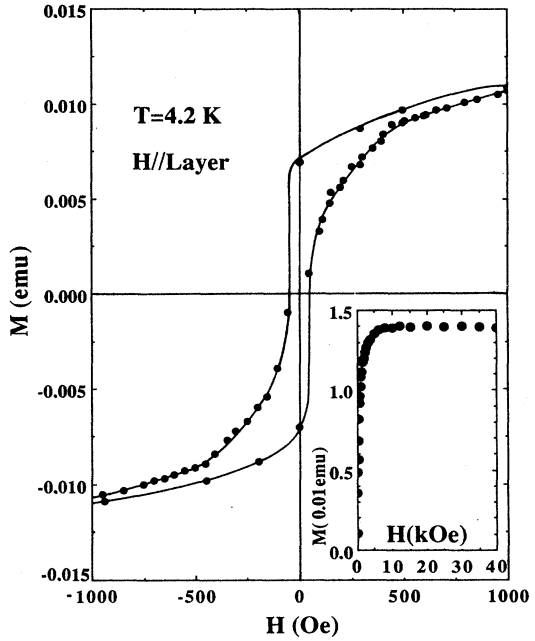

FIG. 3. Hysteresis loop for $[6Co/8Cu]_{62}$ in the range -1 to $+1$ kOe at $T=4.2$ K, magnetic field parallel to the layer. The inset shows the magnetization dependence on higher magnetic fields (until 40 kOe).

measurements.[20] The Co atoms have an average moment similar to the bulk value. At zero field, each Co group is coupled antiferromagnetically to the next group of 6 ML of Co through the intermediate Cu layers. Accordingly, the total magnetization is zero and a new periodicity ($2\Lambda_{SL}$) appears. By increasing the field parallel to the layer a magnetization process starts with a complex behavior for low fields. According to the magnetization and neutron measurements, at 1 kOe the system is only partly antiferromagnetically ordered which explains the low intensity of the satellite corresponding to a periodicity of $2\Lambda_{SL}$, displayed in Fig. 2. Finally, at around 8 kOe all the Co magnetic moments are aligned along the field direction, the saturation magnetization is reached and the magnetic and chemical periodicities (Λ_{SL}) coincide as shown by the complete disappearance of the $\frac{1}{2}$ satellite in the neutron diffraction data at 10 kOe (see Fig. 2).

The next question to be addressed is the magnitude, microscopic origin, and spatial dependence of the interaction between adjacent cobalt arrays giving rise to the observed antiferromagnetic ground state of the superlattice films. Two extreme possibilities are (i) long-range dipolar interaction, i.e., the interaction responsible for domain formation in ferromagnets and (ii) short-range exchange interaction, i.e., a coherent propagation of magnetic correlations across the nonmagnetic Cu layers via an exchange coupling between Co moments and Cu valence electrons similar to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction, as in the case of Gd/Y superlattices.[4] The dependence of the coupling on the thickness of the Cu interlayer (monotonic or oscillatory) could distinguish both mechanisms. Detailed experiments are under way to verify this dependence as well as the complex magnetic structure at low fields.

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[1]For a short, excellent review, see e.g., I. K. Schuller, in *Physics, Fabrication and Applications of Multilayered Structures,* edited by P. Dhez and C. Weisbuch (Springer, Berlin, in press).

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