Two-monolayer oscillations in the antiferromagnetic exchange coupling through Mn in Fe/Mn/Fe sandwich structures

S. T. Purcell, M. T. Johnson, N. W. E. McGee,* R. Coehoorn, and W. Hoving
Philips Research, P.O. Box 80000, 5600 JA Eindhoven, The Netherlands
(Received 22 January 1992)

Oscillations with a period corresponding to two Mn monolayers (ML's) were measured in the antiferromagnetic exchange coupling between ultrathin Fe layers and bulk Fe single-crystal whiskers separated by epitaxial Mn layers. The films were deposited by molecular-beam epitaxy. Electron diffraction showed that the Mn grew monolayer by monolayer in a body-centered-tetragonal structure ($a=2.87$ Å, $c=3.27$ Å) up to 15–25 ML's. The coupling was determined using the magneto-optic Kerr effect. It was antiferromagnetic for all thicknesses above 4–7 ML's Mn, with five strong peaks in the 0–0.2 mJ/m^2 range.

It has been recently found[1–3] that the antiferromagnetic (AF) exchange coupling between Fe layers separated by ultrathin Cr layers oscillates with a period of two Cr monolayers (ML's) in samples with very sharp interfaces. This effect had been sought since the observation of AF coupling in this system by Grünberg *et al.*[4] and subsequent discoveries that the coupling shows several long-period oscillations in magnitude as a function of the Cr thickness, with a period of roughly 15–20 Å.[5] The observation of the two-ML oscillations now permits a much closer comparison between experiments and theoretical calculations based on idealized structures.

Bulk Cr is antiferromagnetic, and this leads one to anticipate that the exchange coupling between the Fe layers may oscillate between AF and ferromagnetic with every Cr ML. However, some theoretical calculations predict these oscillations,[6] while others do not.[7] The calculated coupling values are still an order of magnitude larger than those found in experiment. Measurements of the two-ML coupling oscillations in more than just one system are clearly desirable in order to gain a better understanding of this phenomenon.

Mn is an interesting alternative interlayer to Cr because it also has a tendency to antiferromagnetism. The stable room-temperature phase, α-Mn, is an antiferromagnet with a Néel temperature of 90 K. When Mn is alloyed with small amounts of Fe, Cu, Pd, and Ni and quenched to room temperature, it forms a face-centered tetragonal (fct) lattice and is an AF-I antiferromagnet with Néel temperature $\sim$540 K.[8] In these structures it has a very large moment of $2.3\mu_B$ at room temperature compared to only 0.2 μ_B for Cr.

In this paper we report the experimental discovery of two-ML oscillations in the AF exchange coupling through Mn in the Fe/Mn/Fe system. The coupling was determined in samples similar to those in the Fe-Cr studies.[1,2] They consisted of coherent epitaxial [001] Fe/Mn films, with the Mn in the form of a wedge of varying thickness, grown on Fe[001] single-crystal whiskers. The Mn overlayers were found to have a body-centered-tetragonal (bct) lattice.

Epitaxial Mn layers have been previously deposited by several groups on bcc Fe[001] (Ref. 9) and on fcc Ag[001] (Refs. 10 and 11). Both these lattices have a square surface net with approximately the same lattice parameter (2.8664 Å for Fe and $4.086/\sqrt{2}=2.889$ Å for Ag). It was found that the Mn grew epitaxially with the in-plane spacing and symmetry of both substrates. The perpendicular lattice spacing of the Mn was determined by photoelectron diffraction for the Ag substrate.[11] These measurements showed that Mn formed a bct lattice with $a=2.889$ Å, $c=3.31$ Å, $c/a=1.15$, or, equivalently, a fct lattice with $a=4.086$ Å, $c=3.31$ Å $c/a=0.810$. It was found that the Mn structure was stable to a thickness of 20–25 Å.[10] A careful search by SQUID magnetometry[10] and ferromagnetic resonance[9,10] revealed no detectable magnetic properties of the Mn and it was assumed to be either nonmagnetic or antiferromagnetic. We discuss below the results of band-structure calculations of the magnetism of Mn(bct)/Fe(bcc) multilayers with the measured lattice spacings.

The preparation of the samples and measurement of the coupling is essentially the same as for the Fe-Cr studies described previously.[1] The overlayers were deposited in a multichamber molecular beam epitaxy system (VG Semicon V80M). The growth and structure of the films were monitored by reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED). The Mn wedge shape was formed by slowly moving a shutter across the Fe[001] whisker during evaporation (wedge slope $\cong 0.7$ mm/ML). The substrate temperature was 50 °C during the Mn deposition and room temperature for the Fe. Oscillations in the RHEED intensity that occur during monolayer-by-monolayer growth were also recorded. The position of the start of the Mn wedge relative to the end of the whisker was determined to $\sim$0.1 mm accuracy (0.2-ML Mn thickness) by using an *in situ* scanning electron microscope and Auger electron spectroscopy. The Fe/Mn film was covered with a 20-Å Au overlayer for protection from the atmosphere. The AF coupling strength was determined by analysis of hysteresis loops measured outside the vacuum by the longitudinal magneto-optic Kerr effect. The hysteresis loops were measured as a function

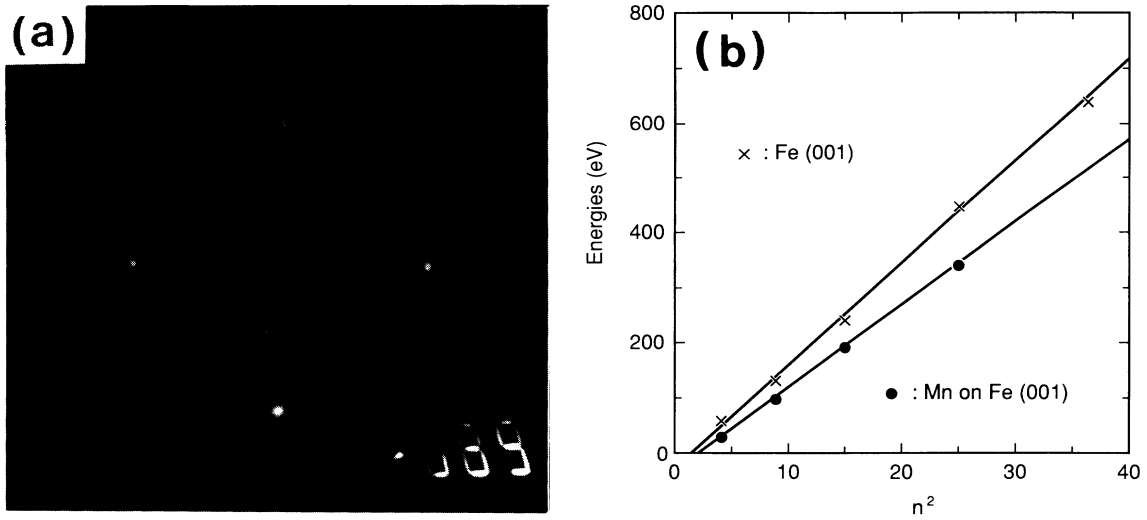

FIG. 1. (a) LEED pattern at 89 eV from an Fe[001] whisker with a 13-ML Mn overlayer. (b) Plot of the energies of the primary Bragg reflections for the Fe[001] substrate and for bct Mn overlayers thicker than six ML's.

of Mn thickness at many positions of the laser spot along the whisker. The thicknesses of the overlayers were such that the Kerr-effect measurement was sensitive to the Fe overlayer and the top of the Fe whisker in a ratio of ~1:3.

In Fig. 1(a) we show a LEED photo at 89 eV from an Fe[001] substrate with a Mn wedge overlayer at a thickness of 13-ML Mn. A comparison of LEED photos at different Mn thicknesses showed that the in-plane lattice spacing and symmetry is the same for the Mn and the Fe. At ~15-ML Mn on this sample the pattern suddenly became much weaker and more complex.

The lattice spacings perpendicular to the surface were determined by measuring the energies of the primary Bragg LEED reflections along the [00] rod. At higher energies these are given quite well by simple kinematic LEED theory. We measured the energies by visually observing the intensity maxima. Plots of these energies versus n^2, where n is the index of the reflection, are shown in Fig. 1(b) for the Fe(001) and the Mn overlayer. The Bragg reflections of the Mn already appeared weakly at approximately four ML's. By fitting the data to straight lines we obtained $c(\mathrm{Fe})=2.88$ Å and $c(\mathrm{Mn})=3.27$ Å. The value of c(Mn) is very close to the value of 3.31 Å found previously using Ag[001] substrates.[11]

In Fig. 2 we show oscillations in the intensity of the specular RHEED beam measured during a growth of Mn on Fe[001] at 50 °C. Though detailed analysis of RHEED oscillations is difficult, such strong oscillations prove that there is substantial completion of single monolayers before the nucleation of the following monolayer. Also visible in the figure is a sudden loss of the oscillations and reflected intensity that marks precisely the onset of the phase transformation, which for this deposition was at the twenty-first ML. This critical thickness is variable from deposition to deposition and may depend sensitively on substrate quality, temperature, cleanliness, and on growth rate. We have found values from 15 to 25 ML's. Also note that there is a slight slip in the amplitude and phase of the RHEED oscillations at approximately two ML's. Such effects are seen in all Mn growths and may be caused by the different perpendicular lattice spacings of Mn and Fe. The effects are not seen for Cr, which has almost the same lattice constant as Fe.[1]

A crucial parameter in epitaxial growth is the lattice misfit between the substrate and possible structures of the overlayer. The misfit can be estimated by considering the overlayer as a distortion of the fct γ-Mn phase, which has lattice spacings of $a=3.782$ Å and $c=3.532$ Å and atomic volume of 12.63 Å^3 for binary Mn alloys when extrapolated to zero solute content.[12] In this case the fct Mn is stretched by 7.2% in-plane and the perpendicular spacing is reduced by 7.1%. We can also consider the room-temperature extrapolation of the lattice constants of the high-temperature bcc δ-Mn phase. This gives a lattice spacing of 2.95 Å, misfit of 3% and atomic volume of 12.88 Å^3. The measured atomic volume in the bct Mn overlayer is 13.44 Å^3, which is significantly larger than

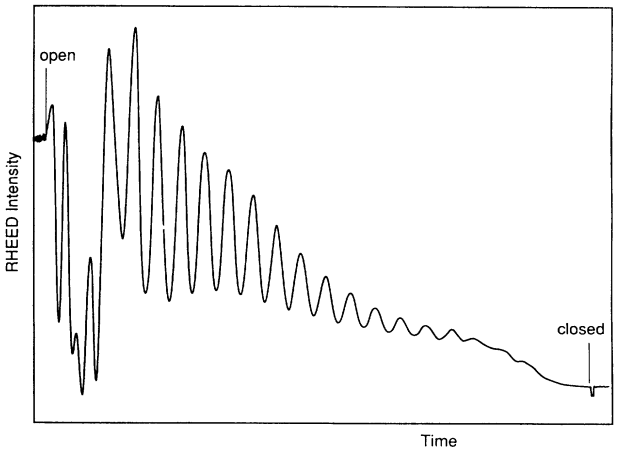

FIG. 2. RHEED oscillations in the specular reflected beam during deposition of Mn on Fe[001] at 50 °C.

for all phases of bulk Mn. In either case these are large lattice mismatches and coherent epitaxial growth would not generally be expected to such thicknesses because of the large elastic energy. The ability of Mn to form tetragonal structures may be the reason for the relative stability of the bct overlayers. Oguchi and Freeman[13] have shown that the antiferromagnetism of γ-Mn stabilizes the tetragonal distortion.

In Fig. 3 we show a hysteresis loop measured by the longitudinal Kerr effect. The large change in the signal near zero field is due to the flipping of the soft Fe whisker magnetization and the other changes are due to the overlayer. As discussed elsewhere[1,14] the shape of these loops can be calculated from simple minimization of the energy including the overlayer anisotropy, field and coupling energies and a partial domain wall in the top surface of the Fe whisker. The form of these loops varies with the relative strength of the magnetic parameters. For medium coupling values they can be characterized by two critical fields in the case of AF coupling: one at which the overlayer magnetization switches away from antiparallel to the whisker magnetization (H_1) and one at which it rotates towards parallel to the whisker magnetization (H_2). Halfway between H_1 and H_2 the overlayer magnetization is approximately perpendicular to the whisker magnetization. For larger couplings (or thinner overlayers) the overlayer magnetization undergoes a more continuous rotation process as a function of field. In this case H_1 approaches zero and the switching fields are not so sharply defined.

In Figs. 4(a) and 4(b) we plot H_1 and H_2 as a function of Mn thickness for two samples. The Fe overlayer thicknesses were $\sim$34 Å for sample 1 and $\sim$60 Å for sample 2. Only H_2 could be determined for sample 1 as H_1 was small and obscured by the hysteresis of the whisker. As can be seen from the figure, the critical fields undergo five strong oscillations in magnitude with a period of two-ML Mn in the measured thickness ranges. The period of the coupling oscillations was within 5% of that given by RHEED oscillations, and the uncertainty in the zero position is $\sim$0.2 ML's. The switching field values are larger for sample 1 than for sample 2 partly because the applied field creates less torque on the thinner Fe overlayer. The minimum thickness at which the AF coupling is present is approximately four ML's for sample 1 and $\sim$7 ML for sample 2. The definition of H_2 is difficult for the thinnest AF region of sample 1 because the overlayer magnetization only gradually approaches saturation. Thus we have only marked this region as AF without quoting field values.

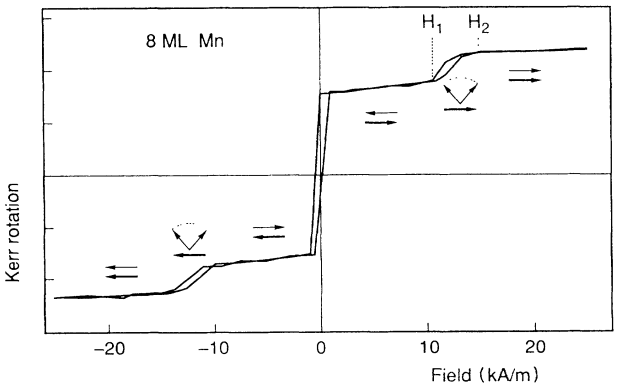

FIG. 3. Longitudinal Kerr hysteresis loop measured from a Au(20 Å)/Fe(60 Å)/Mn wedge/Fe[100] whisker sample. The thicknesses of the Mn was eight ML's. The plane of incidence of the light and the applied field were parallel to the long axis of the whisker. The thin (thick) arrows indicate the direction of the Fe overlayer (whisker) magnetization.

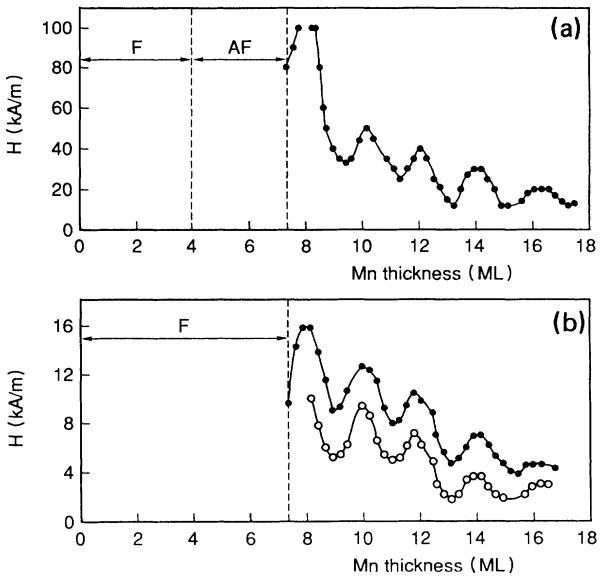

FIG. 4. The Mn thickness dependence of the critical fields, H_1 (○) and H_2 (●) defined in Fig. 3, at which the overlayer magnetization rotates with respect to the whisker magnetization (see text). (a) Sample 1 (34-Å Fe overlayer) and (b) sample 2 (60-Å Fe overlayer). The large oscillations in H_1 and H_2 have a period of two Mn monolayers and correspond to oscillations in the interlayer coupling.

For relatively weak coupling, the coupling parameter J can be approximated by

$$J \cong -d_1(H_1+H_2)M_s/2 ,$$

where d_1 and M_s are the overlayer thickness and magnetization, respectively.[14] Using this expression the couplings can be easily calculated from Fig. 4(b) for sample 2. It is clear that the coupling oscillates with the same period as H_1 and H_2. The value is $J=-0.14$ mJ/m^2 at eight-ML Mn. The expression is less valid for sample 1 because of the strong coupling. However, we can obtain an estimate by using $H_1 \cong 0$. This gives coupling values $\sim$30% higher than sample 2 for thicknesses above nine ML's, suggesting that sample 1 may possess a more ideal interface, a proposal supported by the extension of its AF region to four ML's. Around eight ML's the coupling is still stronger and the approximation becomes progressively worse.

To investigate the origin of the oscillating coupling we have carried out *ab initio* self-consistent band-structure calculations using the augmented-spherical-wave (ASW) method for bct Mn using the measured lattice spacings of the Mn overlayer. The AF-I phase was found to have a

moment of $2.49\mu_B$/atom and 0.153 eV/atom lower energy than the ferromagnetic phase which has $1.22\mu_B$/atom. This calculated AF moment agrees well with values found experimentally[8] and theoretically[13] for bulk γ-Mn. Further ASW band-structure calculations for Fe(five ML)/Mn(seven ML) multilayers showed the AF-I structure of bct Mn with a large Mn moment also exists in multilayers for an odd number of Mn monolayers sandwiched between ferromagnetically aligned Fe layers. Figure 5 shows the calculated Fe and Mn moments, with a parallel and antiparallel Fe-Mn coupling at the interfaces. The parallel coupling was found to be 0.172 eV more stable (per Fe_5Mn_7 formula unit) in contrast to the situation in Fe-Cr systems, where the coupling at the interfaces is calculated to be antiparallel.[7] The calculations were carried out using in-plane spacing, $a = a$(Fe) and the Fe-Fe, Mn-Mn, and Fe-Mn interplaner distances of 1.433, 1.655, and 1.544 Å, respectively. Although two-ML oscillations in the coupling are likely to be related to the AF structure of the bct Mn, explicit calculations are needed to quantify the importance of this term in the coupling energy and to investigate the predominance of the AF coupling above four to seven ML's.

The coupling values found in this study are appreciably smaller than those found in the Fe-Cr case (0.6 mJ/m^2 at eight-ML Cr) despite the much larger calculated moments of the Mn. This might be the result of an intrinsically weaker coupling for Mn or sharper interfaces of the epitaxial Cr layers.

In conclusion, we have grown high quality epitaxial Fe/Mn sandwich structures on Fe[001] whiskers. We have used RHEED and LEED to characterize the Mn structure as bct and to show that monolayer-by-monolayer growth is possible for this metastable structure. Magnetic measurements were made to show the existence of AF coupling in this system. This coupling is antiferromagnetic above a sample-dependent critical thickness of four to seven ML's and oscillates strongly with a period of two Mn monolayers. ASW self-consistent band-structure calculations were used to show that Mn has an AF ground state in hypothetical bulk bct Mn and a Fe-Mn multilayer with the measured lattice parameters.

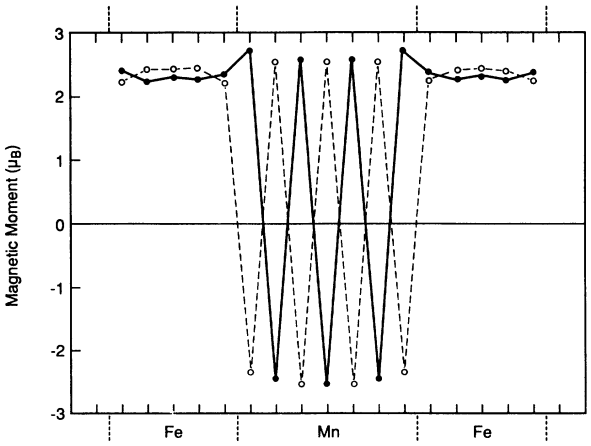

FIG. 5. Calculated spin magnetic moments in a Fe_5/Mn_7[001] multilayer. Solid line: parallel Fe-Mn coupling; dashed line: antiparallel Fe-Mn coupling.

This work was partially supported by the SCIENCE program of the European Community (Contract No. SC1-0387-C of the GP2M3). The authors wish to thank Dr. A. S. Arrott and Dr. B. Heinrich for providing the Fe whiskers and Dr. W. Folkerts for help in interpreting the hysteresis loops.

*Permanent address: Department of Physics, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands.

[1]S. T. Purcell, W. Folkerts, M. T. Johnson, N. W. E. McGee, K. Jager, J. aan de Stegge, W. B. Zeper, W. Hoving, and P. Grünberg, Phys. Rev. Lett. **67**, 903 (1991).

[2]J. Unguris, R. J. Celotta, and D. T. Pierce, Phys. Rev. Lett. **67**, 140 (1991).

[3]S. Democritov, J. A. Wolf, and P. Grünberg (unpublished).

[4]P. Grünberg, R. Schreiber, Y. Pang, M. B. Brodsky, and H. Sowers, Phys. Rev. Lett. **57**, 2442 (1986).

[5]S. S. P. Parkin, N. More, and K. P. Roche, Phys. Rev. Lett. **64**, 2304 (1990).

[6]H. Hasegawa, Phys. Rev. B **42**, 2368 (1990); F. Herman and J. Sticht, J. Appl. Phys. (to be published).

[7]D. Stoeffler, K. Ounadjela, and F. Gautier, J. Magn. Magn. Mater. (to be published).

[8]Cu—D. Megeghetti and S. S. Sidhu, Phys. Rev. **105**, 130 (1957); Ni—G. E. Bacon, I. W. Dunmuur, J. H. Smith, and R. Street, Proc. R. Soc. London, Ser. A **241**, 223 (1957); Pd—T. J. Hicks, A. R. Pepper, and J. H. Smith, J. Phys. C **1**, 1683 (1968); Fe—Y. Endo and Y. Ishikawa, J. Phys. Soc. Jpn. **30**, 1614 (1971).

[9]B. Heinrich, A. S. Arrott, C. Liu, and S. T. Purcell, J. Vac. Sci. Technol. A **5**(4), 1935 (1987).

[10]B. T. Jonker, J. J. Krebs, and G. A. Prinz, Phys. Rev. B **39**, 1399 (1989).

[11]W. F. Egelhoff, Jr., I. Jacob, J. M. Rudd, J. F. Cochran, and B. Heinrich, J. Vac. Sci. Technol. A **8(3)**, 1582 (1990).

[12]W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, London, 1958), pp. 730–735.

[13]T. Oguchi and A. J. Freeman, J. Magn. Magn. Mater. **46**, L1 (1984).

[14]W. Folkerts and S. T. Purcell (unpublished).

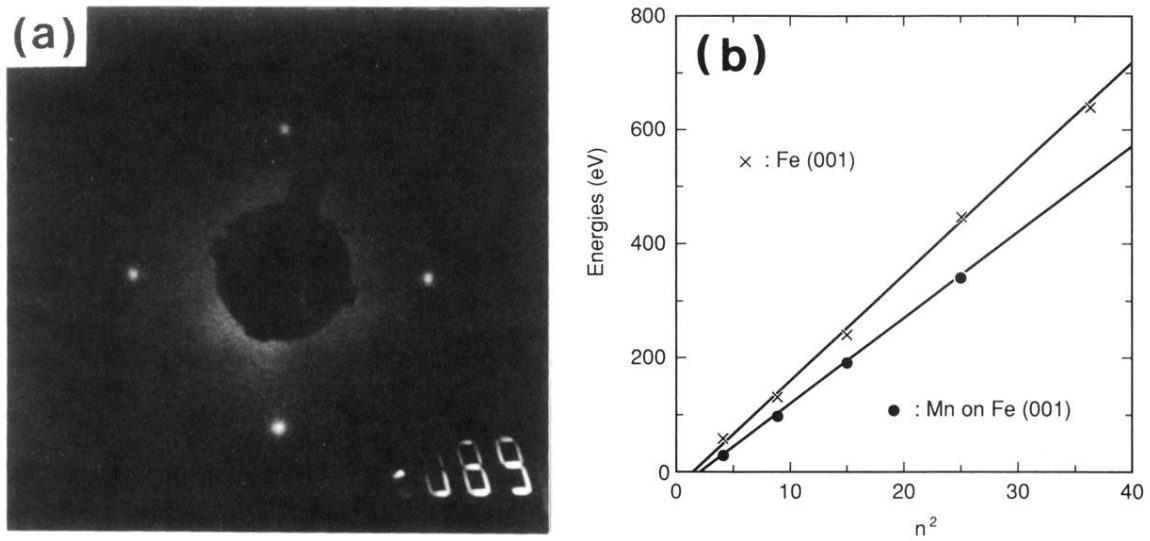

FIG. 1. (a) LEED pattern at 89 eV from an Fe[001] whisker with a 13-ML Mn overlayer. (b) Plot of the energies of the primary Bragg reflections for the Fe[001] substrate and for bct Mn overlayers thicker than six ML's.