Phase transitions in antiferromagnetic superlattices

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We investigate the temperature dependence of the magnetization of films and superlattices of uniaxial antiferromagnets using a self-consistent, mean-field approach and apply the theory to FeF_2/CoF_2 superlattices. The number of magnetic phase transitions in this system (one or two) depends on the thicknesses of the films in the superlattice and on the interface exchange constant. Weak interface coupling leads to two transitions as do thick films. Our findings are in good agreement with recent experimental results and indicate that the FeF_2/CoF_2 system displays strong interface coupling.

The magnetic properties of layered structures may differ markedly from the bulk properties of the constitutive compounds. Magnetic superlattices exhibit features inherent to each of the components and new ones directly associated with the superperiodicity introduced by the alternating stacking of two materials. Also the magnetization may be strongly influenced by size effects, especially for thin-film superlattices.

In the last few years a significant amount of research has been directed to the study of metallic magnetic multilayers. This work has concentrated to a large extent on superlattices with ferromagnetic metals including Fe/Gd,[1-4] Gd/Y,[5] Fe/Cr,[6-8] Co/Ru,[8] and Gd/Dy.[9] A set of results has emerged for these systems whereby a number of magnetic phases can exist and transitions between these phases can be readily introduced by small changes in temperature or applied external fields.

In contrast to the metallic systems discussed above, ionic antiferromagnetic superlattices have only very recently been constructed and studied.[10] Exploring the excellent match between the lattices of nonmagnetic compounds and uniaxial antiferromagnets, a series of magnetic layered structures have been grown and characterized either by antiferromagnetic resonance[11] or thermal expansion[10] measurements. The extremely narrow resonance line of antiferromagnetic films has motivated a series of theoretical studies of radiation transmission under strong static magnetic fields and multistabilities in the transmission as a function of incident radiation frequency were obtained.[12]

In recent measurements[10] on $FeF_2(m$ layers)/$CoF_2(n$ layers) superlattices dramatic size effects were clearly observed. The data displayed either two magnetic phase transitions or one transition depending on the composition m/n. Bulk FeF_2 has a magnetic transition at 78.39 K while CoF_2 has its Néel temperature at 40 K. In thermal expansion measurements on superlattices composed of thicker films $(m/n = 25/30)$ both the high-temperature transition for FeF_2 and the low-temperature transition for CoF_2 were seen. In contrast, for thinner films $(m/n = 19/6)$ only a high-temperature transition is observed.

In many respects antiferromagnetic superlattices differ from the metallic ferromagnetic ones previously studied. The antiferromagnetic system tends to have a more delicate balance between exchange and Zeeman energies as a result of the cancellation of the magnetization of the two sublattices. For example, the zero-field magnetization depends strongly on the superlattice composition m/n and also on the coupling of the two spin systems. In particular, odd/odd and even/even superlattices have a magnetic unit cell identical to the geometrical unit cell, and the first one exhibits a net magnetic moment at low temperatures. The even/even superlattice has no net magnetic moment as a result of the cancellation of the sublattice magnetizations in each film. In contrast, even/odd superlattices have a magnetic unit cell twice as large as the geometrical unit cell and no net magnetization at low temperatures in the absence of external fields.

In this paper we report on a theoretical study of the magnetization of films and superlattices of uniaxial antiferromagnets and make direct contact with the experimental results. We show that the number of phase transitions depends on the interface exchange constant and the thickness of the individual films in the superlattice. Our results show that when the interface exchange is strong and the CoF_2 film is relatively thin, the exchange field from the FeF_2 stabilizes the CoF_2 magnetic structure. Thus only one magnetic phase transition is seen in this case. However, since this stabilizing effect only penetrates a few atomic layers, thicker CoF_2 films are not stabilized in the center of the film and two magnetic phase transitions are seen. Our results are in good agreement with the experimental work[10] and indicate that the interfacial exchange in that system must be fairly strong.

A calculation (or measurement) of magnetization does not always show the presence of the magnetic phase transitions, especially for antiferromagnets where the net magnetization may be zero. We thus calculate the magnetic contribution to the heat capacity which, similarly to the thermal expansion measurement, is sensitive to the phase transitions discussed here.

While there has been some theoretical work[13,14] on phase transitions in antiferromagnetic superlattices, these were for $T=0$ and thus are not appropriate for the recent experiments. We note that there have also been some other theoretical studies on magnetization profiles in thin antiferromagnetic films.[15] These works included dynamic fluctuations and are significantly more involved than the simple mean-field treatment presented here. Nonetheless, these treatments agree with our results—i.e., the magneti-

zation is generally reduced near a free surface—excluding a small oscillation in the magnetization profile found in the dynamic treatment at low temperatures only.

The theoretical method used is similar to that described previously[3] so we only sketch some of the important ideas. We use an iterative, mean-field model which allows for a variation of the magnetization profile as a function of distance from an interface or surface. In essence one begins with an arbitrary configuration giving the magnitude of the spins in each of the layers; the directions are fixed in antiferromagnetic ordering. The energy of spin, S_n, in layer n is calculated as

$$E_n = -g\mu_B S_n H_n \tag{1}$$

where H_n is the effective field produced by the anisotropy, Zeeman, and exchange energies. At finite temperature this field is given by

$$H_n = (Z_{n-1}J_{n-1}\langle S_{n-1}\rangle + Z_{n+1}J_{n+1}\langle S_{n+1}\rangle)$$
$$+ H_a\langle S_n\rangle + H_{ext} \tag{2}$$

where J_{n-1} is the exchange coupling constant connecting the nth layer to the $n-1$th layer and similarly the Z_{n-1} is the coordination number between spins in the nth and $n-1$th layer. $\langle S_n\rangle$ is the thermal averaged value of the spins in the nth layer and is found through the use of the Brillouin function:

$$\langle S_n\rangle = SB_s(E_n/kT) . \tag{3}$$

The problem is, of course, to find a self-consistent set of values $\langle S_n\rangle$. This is done in an iterative procedure. One chooses a layer at random and finds the thermal averaged value for $\langle S\rangle$ in that layer. Another layer is then chosen at random and the thermal averaged value for that layer is also found. The process is then repeated until a self-consistent state emerges. Generally the algorithm works quickly at low temperatures. Near the transition temperature of one of the two compounds, the number of iterations increase and appropriate expansions of the Brillouin function for small arguments are needed.

The parameters used in the calculation are as follows. For FeF_2 the spin is $S=2$, the exchange field is $H_{ex}=434$ kG, and the anisotropy field is $H_a=149$ kG. For CoF_2 the spin is $S=1.5$, $H_{ex}=324$ kG, and $H_a=32$ kG. These values are mean-field parameters and do not exactly match up with measured values obtained through antiferromagnetic resonance. The values used here are those which give the correct transition temperatures for CoF_2 and FeF_2 and which have the correct ratio between exchange and anisotropy fields. The exchange parameters, J, are given by the usual expression $J = g\mu_B H_{ex}/2ZS$ for each material.

Thin antiferromagnetic films display clear size effects. The transition temperatures for the antiferromagnetic film may be reduced by as much as 20%. Generally the bulk transition is regained with a thickness of 15 atomic layers. In Fig. 1, we show the net magnetization for FeF_2 films containing 3, 5, 9, and 21 magnetic ion planes. (Since we always take an odd number of planes here, the films display a net magnetization.) The temperature axis in this figure and the following ones is scaled to the bulk
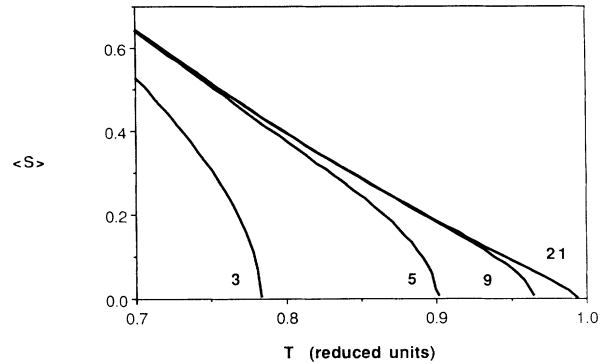

FIG. 1. Average spin value per layer for thin FeF_2 films as a function of reduced temperature $T/T_{Néel}$, where $T_{Néel}$ refers to FeF_2. The numbers by the curves give the number of spin planes for each film.

Néel temperature of FeF_2. It is readily seen that thin films have a reduction in the transition temperature. This reduction is also present in the superlattice case. However, the size effect is reduced by the interface coupling, especially in the strong-coupling limit.

The interaction between the two different antiferromagnetic films in the superlattice is a subject of special interest. In fact, if the compounds have very different bulk Néel temperatures, then one may, or may not, see the low-temperature transition as discussed previously. We explore this feature in Fig. 2 where we plot the calculated magnetization as a function of temperature for a 7/3 FeF_2/CoF_2 superlattice with different values of interface exchange. If the interface coupling is strong, the low Néel temperature compound can be stabilized by the other component of the superlattice, resulting in a much slower decay of the magnetization with temperature. In this case the net magnetization decreases smoothly with temperature and only the high-temperature transition is seen. In contrast, if the interface coupling is weak, the spin systems are effectively independent and two transitions are seen. The low-temperature transition is seen as a rapid increase in the net magnetization for this structure.

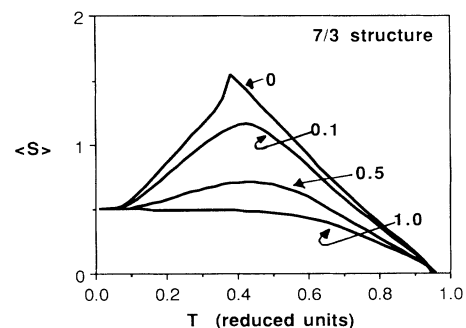It is apparent from the results above that certain phase

FIG. 2. Thermal averaged net spin values per unit cell for FeF_2/CoF_2 superlattice for a 7/3 structure and as a function of temperature for different interface exchange coupling. The numbers give the ratio $J_{interface}/J_{FeF_2}$.
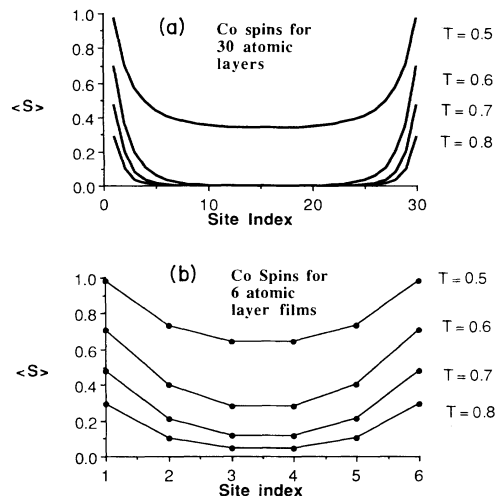
FIG. 3. Absolute value of the CoF_2 spins as a function of position for the FeF_2/CoF_2 superlattice with structures of 25/30 and 19/6. We assume strong interface coupling. Note that the structure with only 6 layers of spins remains in ordered state over the entire temperature range.

FIG. 4. Magnetic contribution to the heat capacity as a function of reduced temperature. For the structures with thicker CoF_2 films, two phase transitions are seen, while for the structures with the thinner CoF_2 films, only one transition is seen.

transitions can be clearly seen in the temperature dependence of the superlattice magnetization. However there is an interesting possibility that does not fulfill this criteria. This is closely related to the antiferromagnetic character of the system and consists of a phase transition involving a set of spins with no net magnetization. For thick CoF_2 films, it is possible for spins in the central part of the CoF_2 film to undergo a phase transition at about the CoF_2 bulk Néel temperature regardless of the value of the interface exchange.

In Fig. 3 we show the CoF_2 spin profiles (magnitude as a function of position) for the 19/6 and 25/30 structures for four selected temperatures. These values are chosen in order to make a direct comparison with the recent experiments. The interfacial exchange was taken to be the FeF_2 value. This represents the strong-coupling limit and effectively means the CoF_2 interface spins are subjected to an exchange field twice as large as the bulk CoF_2 exchange. It is readily seen from Fig. 3 that the two structures behave quite differently. The six CoF_2 spins remain nonzero over the whole temperature range, whereas a major portion of the 25 CoF_2 spins clearly drop to zero at about $T = 0.6$ (46 K). Thus the structure with the thinner CoF_2 film remains in an ordered state well beyond the bulk transition temperature of CoF_2. It is clearly seen that in this case the CoF_2 spins near the interface are stabilized by the exchange coupling to the FeF_2.

The transition discussed above will not be seen in either a calculation or a measurement of the net magnetization of the superlattice. However, it is readily seen in the thermal expansion measurements. We point out that it can also be directly seen by examining the magnetic contribution to the heat capacity. The heat capacity can be easily calculated from our theoretical model once the equilibrium structure is known. One simply evaluates the
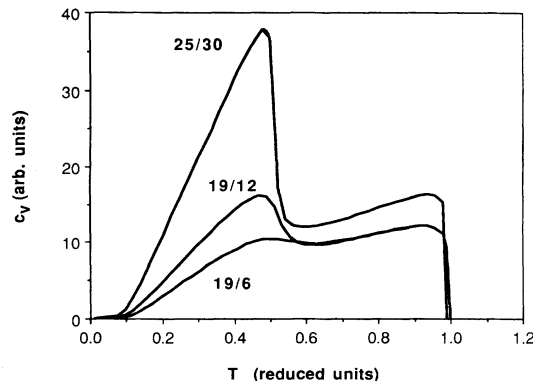
average energy at a given temperature, and then numerically takes the derivative $c_v = dU/dT$ by taking the difference of the energies at nearby temperatures. The magnetic heat capacity for a variety of structures in the strong-coupling limit is shown in Fig. 4. For the structures which have a phase transition (19/12 and 25/30) we see two distinct peaks, each followed by a very rapid decrease in the heat capacity. The sharp decreases are clear manifestations of the high- and low-temperature phase transitions. In contrast, the structure that does not have a phase transition shows a very different behavior, a small rounded shoulder, in the low temperature region where the phase transition might occur.

While a calculation of the thermal expansion coefficient as a function of temperature is beyond the scope of this paper, we note that the behavior of the thermal expansion coefficient is generally similar to that of magnetic heat capacity.[16] The heat capacity curves calculated here do show the same general features seen in the thermal expansion coefficient curves found experimentally, particularly a clear peak for the CoF_2 transition for the superlattices with thicker films and only a rounded shoulder for the superlattices with thinner films.

In summary, the observed features of the FeF_2/CoF_2 superlattices can be readily understood in terms of a simple model. For thin CoF_2 films strong interface exchange coupling can stabilize a few Co spins near the interface and prevent a phase transition. For thicker CoF_2 films a bulk-type phase transition takes place in the center of the film, independently of the value of the interface exchange. We point out that although these phase transitions cannot be seen by a direct measurement of the magnetization, they can be observed in a measurement of the heat capacity.

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