Heat capacity as a probe of surface phase transitions in thin antiferromagnetic films

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External magnetic fields can produce a phase transition from an antiferromagnetic state to a spin-flop state in antiferromagnets. In ultrathin antiferromagnets, the critical magnetic field is sensitive to whether the net number of magnetic layers is odd or even. We show that this transition will produce a distinct feature in the heat capacity as a function of applied magnetic field. The feature is on the order of 5–10 % of the magnetic heat capacity and should be measurable. [S0163-1829(97)06030-X]

The properties of ultrathin magnetic films have been a subject of considerable interest in the last decade. Most of this work has focused on metallic ferromagnetic films, primarily because of the interesting coupling of ferromagnetic films across a nonmagnetic spacer[1,2] and because of the giant magnetoresistance effect.[3,4]

In the last few years, ultrathin antiferromagnetic multilayers[5,6] and thin films[7,8] have also been constructed and studied. Such materials are interesting both for fundamental and technological reasons. In contrast to the metallic ferromagnetic systems, the antiferromagnets are generally insulators and thus the simpler localized spin models should be more appropriate. Furthermore, the antiferromagnetic system has many fundamental differences with ferromagnets. The magnetic structure is clearly more complex and allows a larger number of stable configurations. Also, the anisotropy field in antiferromagnets can be quite large, on the order of several hundred kG, compared to the 1–2 kG typically found in the ferromagnetic metals. In terms of technological use, antiferromagnets and their coupling to ferromagnets are fundamental to the giant magnetoresistance spin-valve structures which will be vital to the next generation of reading heads in hard-disk systems.

Since antiferromagnets have a magnetic structure which can change significantly from layer to layer, high-quality samples are of particular importance. For example, one can consider an antiferromagnet with all the spins in one layer, parallel to the surface, pointing in the same direction, but where the spins in the neighboring layers (above and below) all point in the opposite direction. Such a structure has very different properties depending on whether the total number of magnetic layers is odd or even. For an even number of layers there is no net magnetic moment, while for an odd number of layers one of the spin sheets is uncompensated and a net magnetic moment results.

A particularly exciting experimental development is the recent observation of clear oscillations in the magnetization of thin antiferromagnetic films as a function of the thickness of the film.[7] These experiments provide evidence that high-quality antiferromagnetic films, with a well-defined number of magnetic layers, can now be grown and studied. Furthermore, these experiments indicate that the magnetic structure of ultrathin antiferromagnets may differ considerably from that of the bulk. For example, in Ref. 7 it was reported that the magnetic moments in a thin film of CoO were parallel to 100 planes. This is in sharp contrast to the known bulk structure where the magnetic moments lie parallel to 111 planes.

One consequence of having such high-quality films is that one may examine the effect finite-size effects have on magnetic phase transitions.[7,9,10] This is particularly interesting because in antiferromagnets some of the finite-size effects depend on whether the number of magnetic layers is even or odd. This is in distinct contrast to ferromagnets. For example, a sufficiently large external magnetic field will cause a phase transition from the antiferromagnetic state to a spin-flop (or canted) structure. In thin antiferromagnetic films the critical field necessary strongly depends on whether there is an uncompensated layer of spins or not.

The purpose of this paper is to show theoretically that the different kinds of phase transitions may be observed by making heat capacity measurements as a function of applied magnetic field. We note that heat capacity measurements or related measurements such as thermal expansion have been used frequently in characterizing antiferromagnetic thin films and multilayers.[5,8] Our results indicate that the phase transitions should show a distinct feature in the heat capacity. Furthermore, the feature is on the order of about 6–10 % of the magnetic heat capacity itself and thus should be able to be measured readily.

We use the self-consistent local field method developed earlier and applied to a number of different magnetic superlattices and antiferromagnetic films.[11] In this method one simply calculates the total effective field (the sum of the exchange field, the anisotropy field, and the external field) acting on an individual spin. This spin is then rotated in such a way as to minimize its energy. This is done for each spin in the structure and repeated until a stable configuration appears. To take into account thermal effects, the Brillouin function is used to give the thermally averaged magnitude of the spin in a total effective field at a given temperature T. The heat capacity can be easily calculated once the equilibrium structure is known. One simply evaluates the average energy at a given temperature and then numerically takes the derivative $C_V=(\partial U/\partial T)_V$ by taking the difference of the energies at nearby temperatures.

We consider a thin antiferromagnetic film, with parameters generally characteristic of MnF_2 with the easy axis parallel to the surface. An external magnetic field H_0 is also oriented parallel to the surface and along the easy axis. We take the magnetic structure to consist of sheets of spins, ori-

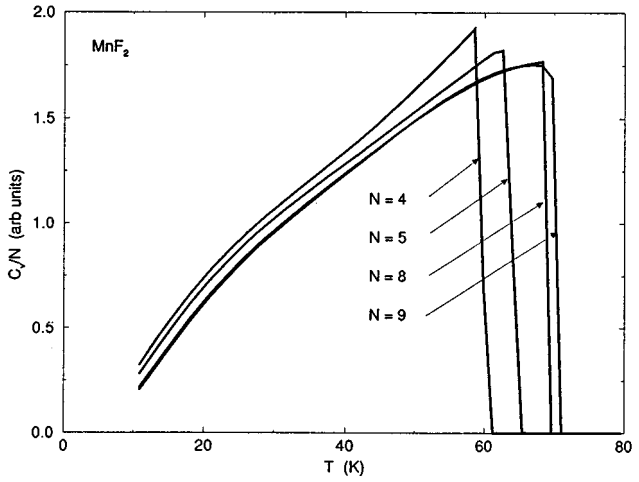

FIG. 1. Normalized heat capacity as a function of temperature for different numbers of magnetic layers in a thin antiferromagnetic film. The different transition temperatures for different N are due to finite-size effects.

ented parallel to the surface, with the spins on one plane antiparallel to those on the neighboring planes. We consider systems with the number of magnetic planes, N, being both odd and even. The parameters are $H_e=46.7$ T for the exchange field and $H_a=0.7$ T for the anisotropy field. We will also look at a MnF_2-like material where all the parameters are the same as in MnF_2 except that the anisotropy field has been increased by a factor of 2.

In Fig. 1 we present the normalized heat capacity (C_V/N) as a function of temperature for films with different numbers of layers. The most prominent feature is that the transition temperature is strongly dependent on the number of layers and decreases as the number of layers is decreased. This is a clear result of finite-size effects; i.e., the reduced coordination of the spins at the surfaces results in a smaller effective field for those spins. This in turn means that the surface spins are more susceptible to thermal agitation and the thermal averaged magnitude of these spins is reduced from what is expected in the bulk. For very thin films, this reduction propagates through the entire structure and the transition temperature is also reduced. The change in the critical temperature as a function of the number of magnetic layers is in good qualitative agreement with recent experiments on CoO.[8]

When the thickness of the film reaches $N=8$ and $N=9$, the heat capacity curves are nearly the same. There is a near-linear increase in heat capacity as T increases and a leveling off and a rapid drop at the transition temperature. (We note that for a bulk sample in the mean-field approximation the linear region extends directly to the phase transition. The leveling off, which can be seen in experimental data, occurs here because of finite-size effects.) The only difference between the $N=8$ case and the $N=9$ case is that the transition temperature is slightly higher for $N=9$ since finite-size effects play a smaller role for larger systems.

In contrast to the results above, the heat capacity as a function of applied field shows a striking difference between a structure with an odd number of layers and one with an even number of layers. In Fig. 2(a) we show heat capacity as

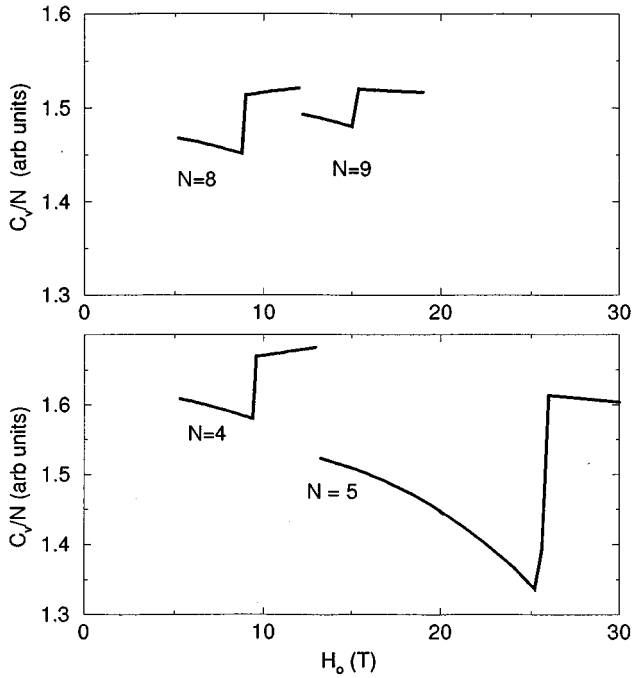

FIG. 2. Normalized heat capacity as a function of magnetic field for different numbers of magnetic layers. Thicker films are shown in (a) and thinner ones in (b). The phase transition of films with N even are much lower than for those with N odd.

a function of applied field for a temperature of 50 K for thicker films ($N=8$ and $N=9$), while in Fig. 2(b) we examine the field dependence for thinner films. The system with an even number of layers shows a rapid change in heat capacity at a low field, while the system with an odd number of layers shows a similar change at much higher fields. For the thicker films the relative change in C_V is on the order of 4%. For the thinner films the relative change is on the order of 6–10 %.

The origin of this behavior is due to a phase transition from the antiferromagnetic state to a spin-flop state where the spin moments are canted with respect to the applied field as shown in Fig. 3. The magnetic structure, of course, is determined by finding the state which minimizes the sum of the Zeeman energy, the anisotropy energy, and the exchange energy. In the antiferromagnetic state and with N even, the net Zeeman energy is zero, with as many spins pointing opposite to the field as there are spins pointing parallel to the field. As the external magnetic field is increased, the structure can lower its energy by changing to the canted configuration seen in Fig. 3(b), where each magnetic moment has a component parallel to the applied field. This change in configuration comes with an increase in exchange and anisotropy energies, but this is overcome by the lowering of the Zeeman energy.

It has been known for many years that the magnetic-field-induced transition at $T=0$ to a spin-flop state in a large (bulk) structure occurs at a critical field given by

$$H_{\text{bulk}}=\sqrt{2H_eH_a+H_a^2}. \tag{1}$$

In addition to the bulk spin-flop transition, surface-induced spin-flop transitions have also been predicted.[12] In that work

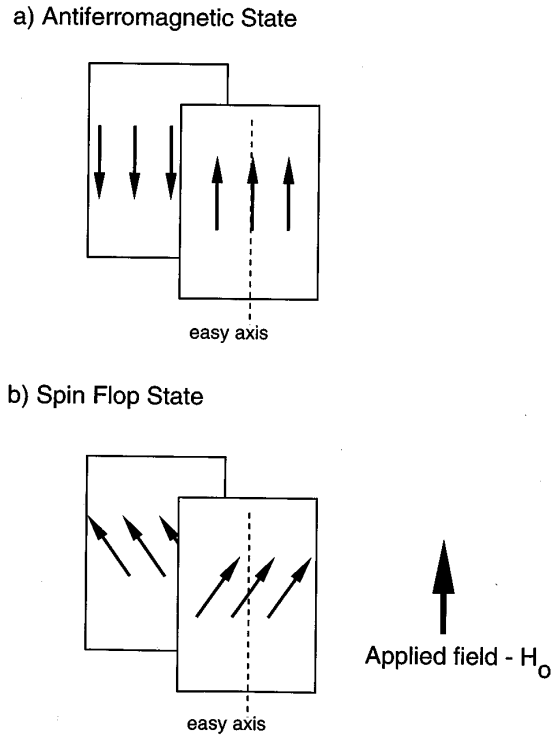

FIG. 3. Illustration of the antiferromagnetic state and spin-flop state geometry. The applied field is applied parallel to the easy axis.

it was shown that the antiferromagnetic phase would become unstable at a field which was considerably lower than that of the bulk critical field. The critical field for this surface transition at $T=0$ is given by

$$H_{\mathrm{surf}}=H_{\mathrm{bulk}}/\sqrt{2}. \tag{2}$$

Keffer and Chow later showed that the surface flop would evolve into a bulk spin-flop state as the magnetic field was increased.[13] Although the precise validity of these results has been challenged recently,[14] experimental results on metallic multilayers with ferromagnetic films coupled antiferromagnetically through a nonmagnetic spacer film[15] have indeed shown that a surface spin flop takes place at approximately the value given by Eq. (2).

In thin films the critical field is further modified by surface effects.[16] When the number of magnetic layers is odd, there is a net magnetic moment for the antiferromagnetic thin film. If we put an applied field along the easy axis, this moment will be parallel to the field, and thus the Zeeman energy will not be zero in the antiferromagnetic state. As a result, the transition from the antiferromagnetic state to the spin-flop phase, which in the bulk material is associated with a change in Zeeman energy from zero to some negative value, is inhibited since the antiferromagnetic state already has a negative energy contribution from the Zeeman energy. In contrast, in a thin film in the antiferromagnetic state with an even number of layers has no Zeeman energy when an external magnetic field is applied along the easy axis. As a result, the system can more easily take advantage of the lowering of the energy produced by the spin-flop transition and the phase transition occurs at a much lower applied field.

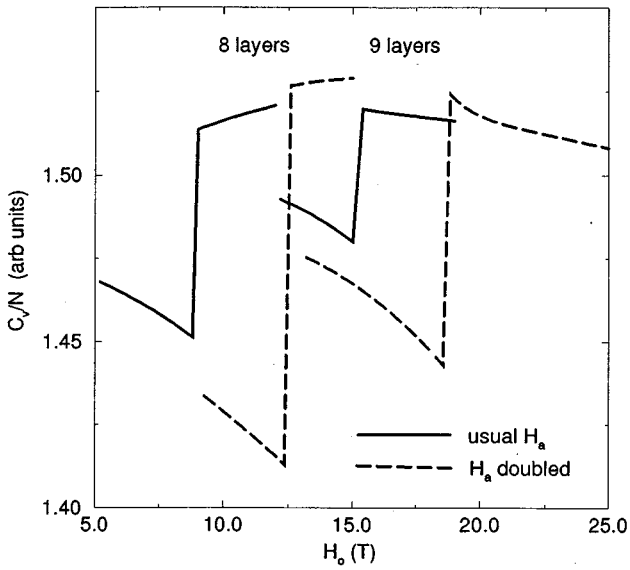

FIG. 4. Normalized heat capacity as a function of field for $N=8$ and $N=9$. The solid lines indicate the results for MnF_2, and the dashed lines show the results for a material with MnF_2 parameters except that the anisotropy field has been doubled.

This behavior helps to explain a very interesting result to be found in Fig. 2. We note that the jump in the heat capacity occurs at about the same critical field when the number of layers is even. When the number of layers is odd, the critical field is much larger for the thinner antiferromagnetic film.[16] The key issue is that the Zeeman energy in the antiferromagnetic state always comes from only one uncompensated plane of spins for any structure where N is odd. In contrast, all the other energies (exchange and anisotropy) scale linearly with the number of layers. Thus the Zeeman energy associated with the uncompensated layer (and it is this which inhibits the phase transition) becomes less important as N increases. As a result, the critical field for the phase transition is reduced as N is increased.

We comment briefly on the numerical values in Fig. 2. With the parameters for MnF_2, one expects the bulk spin-flop transition at $T=0$ to occur at an external field of $H_0=8.1$ T. The transitions here, for both N even and N odd, at $T=50$ K lie above that value. This is consistent with recent theoretical calculations exploring the temperature-field phase diagram for thin antiferromagnetic films which showed that the critical field for a transition to the canted state rises as the temperature rises.[16]

We have also calculated the heat capacity at lower temperatures. The percentage shift in the heat capacity at the phase transition decreases as T decreases, except for the case of very low temperatures and N even. Since the heat capacity is significantly lower at lower T (as seen in Fig. 1), this is likely to be a more difficult measurement.

It is of interest to see how the size of the jump in the heat capacity depends on the characteristic material parameters. In Fig. 4 we explore the spin-flop transition for a material with parameters closer to that of MnF_2, but where the anisotropy field has been increased by a factor of 2. We see that for both an even and odd number of layers the phase transition

occurs at a higher field as might be expected from Eqs. (1) and (2). In addition, the shift in the heat capacity is larger in both cases.

In summary, we have explored whether the spin-flop phase transition in thin antiferromagnetic films can be observed by heat capacity measurements. It was shown that the spin-flop transition is accompanied by a jump in heat capacity which was on the order of 6% of the heat capacity itself. In contrast to heat capacity measurements made in zero field, films with an even and an odd number of layers behave very differently. Films with an even number of layers have transitions which occur at fields below that of the bulk phase transition. Films which have an odd number of layers have a transition which occurs well above the critical field for the bulk transition.

In real films, of course, the number of layers will not be constant over an entire film. In that case a heat capacity measurement may be a way of characterizing the magnetic structural quality. For example, if the regions where a well-defined number of layers exist are reasonably large, one might find two jumps in heat capacity as a function of field, one at higher field corresponding to an odd number of layers and one at lower field corresponding to an even number of layers. If the spatial regions of a well defined number of layers are small, then presumably one sees only one phase transition where the entire structure changes together at some average field.

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