# Thermodynamic Measurements of Magnetic Ordering in Antiferromagnetic Superlattices

E. N. Abarra,[1] K. Takano,[1,2] F. Hellman,[1] and A. E. Berkowitz[1,2]
[1]*Department of Physics, University of California, San Diego, La Jolla, California 92093*
[2]*Center for Magnetic Recording Research, University of California, La Jolla, California 92093*
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Direct measurements of heat capacity from 80 to 540 K of antiferromagnetic superlattices of NiO (high Néel temperature $T_N$), CoO (low $T_N$), and MgO (nonmagnetic) are used to study the effect of exchange coupling and layer thickness on magnetic ordering. NiO/CoO superlattices with thin layers show a single heat capacity peak similar to a $Ni_{0.5}Co_{0.5}O$ alloy; with increasing layer thickness, the peak splits into two maxima. Finite size effects are seen in uncoupled NiO and CoO. Observed shifts in $T_N$ show the importance of correlation lengths and spin fluctuations in the ordering. [S0031-9007(96)01343-9]

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Interest in thin films and superlattices of antiferromagnetic (AFM) insulators such as $CoF_2$ [1] or NiO [2] has grown, for both fundamental studies and device applications [3]. The localized moments, short-range nature of the exchange interaction, and simple magnetic anisotropy make these materials, in principle, easier to model than metallic magnets [1]. Thus, several AFM insulators have been fabricated in layered structures such as $CoF_2/FeF_2$ [1], $FeF_2/ZnF_2$ [4], and NiO/CoO [2]. Previous measurements by exchange-induced anisotropy [5] and neutron scattering [6] on NiO/CoO superlattices have shown interlayer magnetic coupling of the NiO layers at temperatures well above the Néel temperature $T_N$ of CoO despite the short range of the superexchange interaction, consistent with mean field calculations [7]. Thermal expansion coefficient $\alpha(T)$ measurements using high-resolution x-ray diffraction found similar results on $CoF_2/FeF_2$ superlattices [1]. Large finite size effects for $FeF_2$ layers with nonmagnetic $ZnF_2$ interlayers have also been observed using thermal expansion [4] and more recently for CoO/$a$-$SiO_2$ multilayers by magnetic susceptibility measurements [8].

In this Letter, we report the first direct measurement of the specific heat of magnetic superlattices. These measurements are made possible by the use of our novel microcalorimeters [9] and are unique in that they involve thin films (10 $\mu$g mass) of materials with high $T_N$ where specific heat measurements are extremely difficult. Magnetic measurements of very thin films of AFM materials may be complicated by the response of the uncompensated spins at the surfaces or interfaces. Heat capacity measurements are not subject to this concern. NiO, CoO, and MgO all form in the NaCl structure. $T_N$ for NiO and CoO are 523 and 293 K, respectively. MgO is nonmagnetic. Using the specific heat of NiO/CoO, CoO/MgO, and NiO/MgO superlattices, the effects of exchange coupling across the interfaces and finite size are studied from a thermodynamic viewpoint. Analysis of the temperature dependence of the specific heat, available for the first time here, should provide quantitative tests of models for magnetism in superlattices and thin films.

Heat capacity measurements of *microgram* thin films up to 540 K are made possible by the drastic reduction of the contribution of the addenda (substrate, thermometer, and heater) to the total heat capacity. The substrate for these samples is a 310 nm thick amorphous silicon nitride ($a$-Si-N) membrane with a thin film heater and thermometer deposited on one side. NiO, CoO, $Ni_{0.5}Co_{0.5}O$, and MgO were reactively sputtered from separate Ni, Co, NiCo alloy, and Mg targets directly onto the other side of this membrane. A 200–250 nm overlayer of Ag (or Al) is used to ensure a high internal thermal conductivity, as discussed in Ref. [9]. Deposition conditions and structural characterization of single crystal NiO and CoO films and NiO/CoO superlattices on sapphire substrates are published elsewhere. The samples were shown to possess coherent crystalline structures with interdiffusion and surface roughness less than a monolayer [10,11]. The $a$-SiN substrate of the specific heat devices leads to polycrystalline films with an in-plane grain size of 25–50 nm; strong (111) texture and structural coherence through many layers is observed. A set of NiO/CoO multilayers were made with bilayer thicknesses $\Lambda = 2.6$, 5.0, 7.6, and 9.6 nm; the NiO:CoO thickness ratio is held fixed at 1:1. The total thickness for these films is 250 nm. For comparison with the superlattices, we also grew a $Ni_{0.5}Co_{0.5}O$ alloy, and pure NiO and CoO.

High angle x-ray diffraction (XRD), low angle x-ray reflection (XRR), and cross-section transmission electron microscopy (TEM) were used to characterize the samples, using samples on $a$-Si-N substrates from the same deposition. Values for the (out of plane) lattice constant $d$ determined from high angle XRD for NiO and CoO films are 0.421 and 0.427 nm, respectively. For $Ni_{0.5}Co_{0.5}O$, $d = 0.425$ nm from the (111) peak and $d = 0.424$ nm from the (220) peak. Both NiO and $Ni_{0.5}Co_{0.5}O$ are expanded out of plane and compressed in plane. CoO has a (111) texture while NiO and $Ni_{0.5}Co_{0.5}O$ share a (110) texture. By growing CoO as the first layer, we obtain NiO/CoO superlattices with a (111) texture. XRD shows a single set of peaks with $d = 0.425$ nm out of plane and

0.422 nm in plane. XRD patterns for $\Lambda = 2.6$–$9.6$ nm films show the (111) reflection and satellite peaks consistent with the multilayer structure. For the $\Lambda \geq 5.0$ nm samples, the first and third order superlattice peaks of the low angle XRR scans are clearly visible; the second and fourth order peaks are suppressed as expected for multilayers with constituents having similar scattering factors and identical thicknesses. For the $\Lambda = 2.6$ nm sample, the first order peak is clear; the next (third order) peak is outside the range of the XRR measurement. Further quantitative refinement of the data is complicated by the similarity of the CoO and NiO scattering factors.

Low angle XRR and high angle XRD scans give $\Lambda$ values in agreement with each other and with growth parameters. The structural coherence length $\xi$ obtained from the full width at half maximum of the central peak of the superlattices is ~23 nm, although cross-section TEM suggests coherence extending through the entire thickness of the films. Consistent with earlier structural work on single crystal NiO/CoO superlattices, we observe oscillating stress gradients due to the lattice mismatch between NiO and CoO of period $\Lambda$ from TEM which argues for coherence along the plane of the interfaces [11].

Several CoO($t_c$)/MgO($t_m$) and NiO($t_n$)/MgO($t_m$) superlattices were also grown with layer thicknesses $t_c$ and $t_n$ from 1.6 to 10.2 nm and $t_m = 0.9$ to 4.4 nm. MgO has $d = 0.421$ nm. High angle XRD patterns for CoO/MgO superlattices show the (111) and (220) reflections and the accompanying satellite peaks; $d = 0.425$–$0.427$ nm. The width of both the (111) and the (220) reflections yields $\xi = 25$ nm (many bilayers). Low angle XRR scans show many peaks indicating the compositional modulation. We obtain comparable results for NiO/MgO multilayers with $d = 0.422$ nm.

Figure 1 shows the specific heat of NiO and CoO from 80 to 530 K, in good agreement with bulk literature data [12] except for a rounding of the CoO peak which we attribute to reduced crystallite sizes (30 nm). The inset shows the heat capacity of CoO and the addenda. The total heat capacity at 500 K is ~20 $\mu$J/K and the addenda, including the contribution of the Ag conducting layer, is ~11 $\mu$J/K. Therefore, even at elevated temperatures, the signal from ~12 $\mu$g of oxides is large. To determine the addenda contribution, we measured the heat capacity of Ag deposited on a separate microcalorimeter processed from the same wafer; the variation in the addenda within a single wafer of devices is experimentally observed to be ~3% [9].

The magnetic contribution to the specific heat $c_m$ is obtained by subtracting the lattice contribution from the total sample specific heat. For the alloy and the NiO/CoO superlattices, the lattice contribution is calculated from that of NiO and CoO, weighted according to volume. This lattice contribution is determined by fitting the low temperature specific heat of NiO and CoO to Debye and Einstein functions [13]. For temperatures ≥300 K, there is a significant anharmonic (dilation) contribution [14]. This is linear with temperature far below the melting point and may be determined from bulk modulus values; these, however, are scarce for temperatures other than room temperature. Instead, we estimated the dilation contribution to the lattice specific heat by constraining the integrated magnetic entropy $S_m$ to $R \ln 3$ for CoO [15] and $R \ln 2$ for NiO [16]. The total lattice contribution is a smooth monotonic function (the small contribution from the lattice distortion at $T_N$ is ignored).

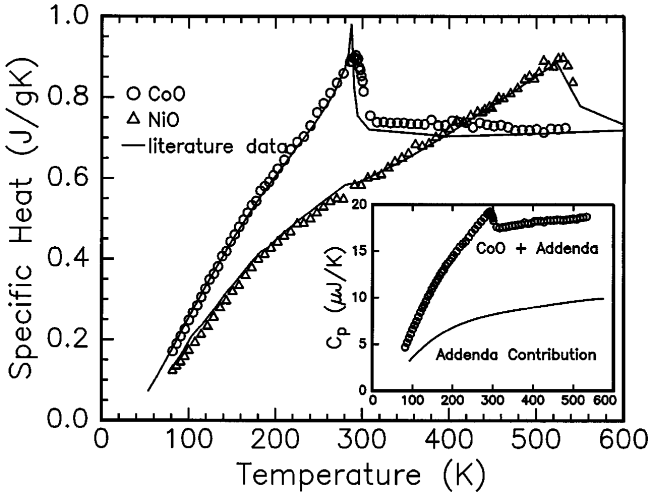

FIG. 1. Specific heat of CoO (circles), NiO (triangles), and previously published data for bulk CoO and NiO (solid line) (Ref. [12]). Inset shows total measured heat capacity (CoO + addenda) (circles), and addenda alone (solid line).

Figure 2(a) shows $c_m$ of the thinnest bilayer sample ($\Lambda = 2.6$ nm) and the $Ni_{0.5}Co_{0.5}O$ alloy. Instead of observing two peaks corresponding to CoO and NiO we observe one broad peak at 400 K. The temperature dependence of $c_m$ is virtually identical to that of the homogeneous alloy despite the structural evidence of layering. Figure 2(b) shows $c_m$ for samples with $\Lambda \geq 5.0$ nm. $c_m$ for these thicker layers shows two broad maxima between the $T_N$ of CoO and that of NiO. The maximum at higher temperature corresponds to the ordering of the NiO layers while the peak at lower temperature corresponds to the rapid increase in CoO moments. Exchange coupling suppresses the ordering temperature of NiO but raises the temperature of the peak associated with CoO [7]. These results are consistent with earlier dilatometric measurements on $CoF_2/FeF_2$ superlattices [1].

Figure 3(a) shows the specific heat for several thicknesses of CoO extracted from the specific heat of CoO/MgO multilayers (MgO contribution subtracted). The peaks broaden and $T_N$ clearly shifts to lower temperatures with decreasing layer thickness, although by far smaller values than recently reported for multilayers of CoO/$a$-$SiO_2$ (e.g., in that work, $T_N = 25$ K for $t_c = 1.5$ nm) [8]. These earlier results were based on magnetic susceptibility, which for thin films may

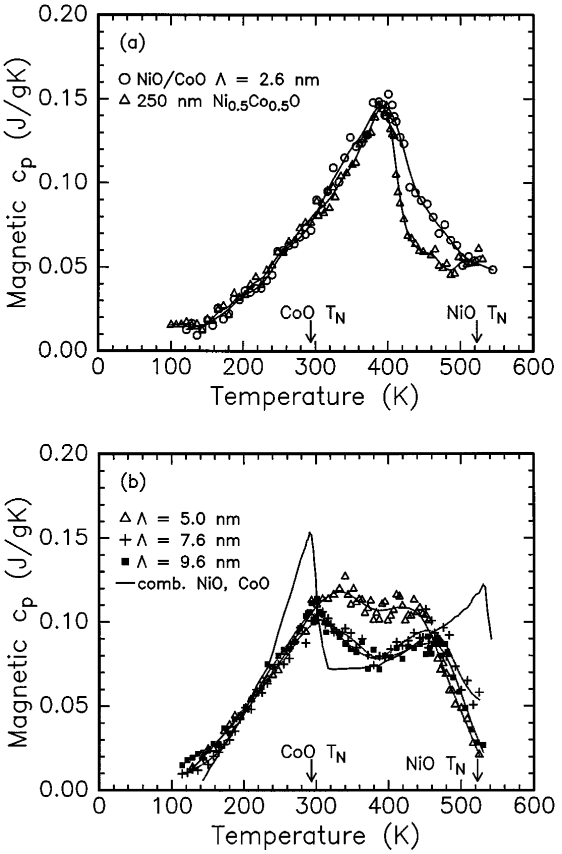

FIG. 2. Magnetic specific heat of (a) $\Lambda = 2.6$ nm superlattice (circles) and $Ni_{0.5}Co_{0.5}O$ alloy (triangles), and (b) of a series of NiO/CoO superlattices.

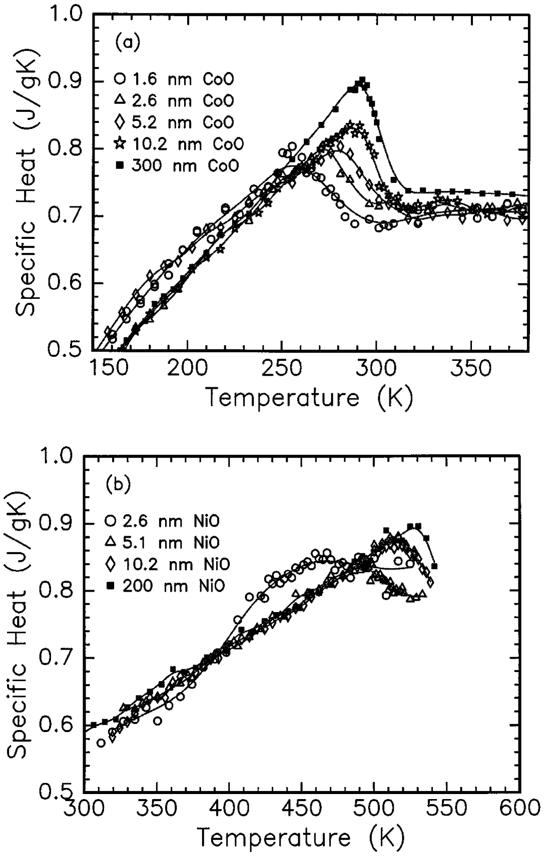

FIG. 3. Magnetic specific heat of several thicknesses of (a) CoO from CoO/MgO multilayers and pure CoO thin film, and (b) NiO from NiO/MgO multilayers and pure thin film.

be unduly influenced by uncompensated surface spins. We have tested our results for unintentional coupling between layers (due, for example, to pinholes) which might artificially increase $T_N$. First, specific heat was measured for CoO/MgO multilayers with $t_c = 2.6$ nm and $t_m$ increased to 4.4 nm; $c_m(T)$ is identical to the $t_m = 1.6$ nm sample. Second, from neutron scattering, we find the magnetic correlation length to be confined to one layer [17].

Figure 3(b) shows similar data for NiO from NiO/MgO multilayers. The peaks are noticeably more rounded and $T_N$ is suppressed considerably more than for CoO layers of comparable thickness. Both effects are possibly due to the lower anisotropy energy of NiO. $T_N$ is less suppressed here than for comparably thick NiO layers exchange coupled to CoO. A similar result was found in the $CoF_2/ZnF_2$ superlattices when compared with $CoF_2/FeF_2$ [4].

Strain intrinsic to the sputtering process and due to the lattice mismatch between layers could, presumably, shift $T_N$. We suggest that for NiO and CoO, uniaxial strain up to 2% (as opposed to hydrostatic compression) has little or no effect. A sample with 10.2 nm layers of NiO is measured to be under substantial compression (1.5%), but we observe little shift in $T_N$ from the bulk value. Moreover, two CoO(2.6 nm)/MgO [as well as two NiO(2.6 nm)/MgO] superlattices with different $t_m$ are differently strained yet exhibit the same $T_N$. The shifts in $T_N$ are, therefore, primarily due to exchange coupling and/or finite size effects.

$S_m$ for the NiO/CoO superlattices at 530 K is $\frac{1}{2}R(\ln 3 + \ln 2)$ to within 30% [15,16]. The 30% uncertainty arises from the 3% uncertainty in the addenda. Samples with thicker bilayers develop entropy at lower temperatures indicating that the NiO moments are not stabilizing the CoO moments as well. The thin layered superlattice behaves like the alloy. Determination of the entropy for CoO and NiO from the CoO/MgO and NiO/MgO multilayers is undependable due to the smaller total magnetic layer sample masses involved than in the NiO/CoO superlattices.

Figure 4 summarizes the peak positions of the specific heat vs the magnetic layer thickness. In the NiO/CoO superlattices, for individual layer thicknesses of 1.3 nm, NiO and CoO order at one temperature between the $T_N$ of bulk NiO and CoO, matching the $Ni_{0.5}Co_{0.5}O$ alloy. For thicknesses of 2.5 nm, we observe two maxima in the specific heat, at temperatures still shifted from the bulk

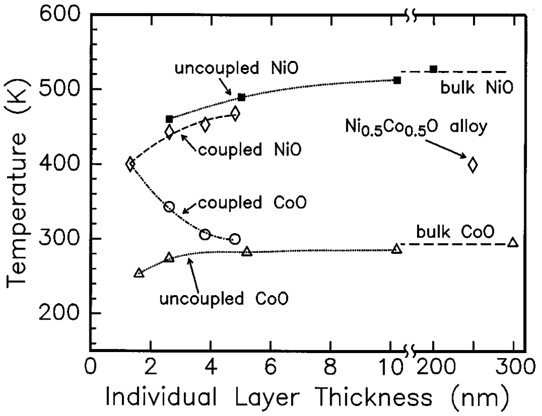

FIG. 4. Temperature dependence of the specific heat maxima with layer thickness for exchange coupled NiO/CoO and NiO and CoO (with MgO interlayers).

values. These show that the intrinsic magnetic correlation length for CoO or NiO is between 1.3 and 2.5 nm. For uncoupled CoO, $T_N$ starts to be shifted to lower temperatures near approximately $t_c = 2.6$ nm, but even for $t_c = 1.6$ nm is within 35 K of the bulk value. For uncoupled NiO layers, $T_N$ is suppressed more than CoO, for comparable thicknesses. However, the suppression in $T_N$ is greater when NiO is coupled to CoO than when isolated with MgO on either side, a result we suggest is due to spin fluctuations in the CoO at the NiO/CoO interface. The CoO $T_N$ is similarly substantially more enhanced by exchange coupling to NiO than it is suppressed when isolated with nonmagnetic MgO. The above results are incompatible with a simple summing up of pairwise exchange interactions in a mean field type model.

In summary, we have successfully measured the heat capacity of various AFM oxide superlattices to study the effect of exchange coupling and finite size. Superlattices consisting of thin AFM layers with two different $T_N$ order identically to an alloy while comparable thickness superlattices consisting of AFM layers with intervening nonmagnetic layers order at a temperature only slightly suppressed from the bulk $T_N$. These results demonstrate the importance of considering correlation lengths and spin fluctuations in the magnetic ordering even of AFM insulators rather than a simple interneighbor exchange interaction model.

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[16] At 600 K, we expect two accessible states for $Ni^{2+}$. This is consistent with measurements of low temperature ($T <$ 100 K) and high temperature ($T = 700$ K, Ref. [13]) specific heat which constrain the magnetic entropy to $R \ln 2$.
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