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Observation of Interfacial Electrical Polarization in Fe_3O_4/NiO Superlattices

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The dielectric permittivity of Fe_3O_4/NiO superlattices reveals frequency-dependent features, not found in the constituent materials, which we identify as due to interfacial (Maxwell-Wagner) electrical polarization. Large modulations of the displacement field within 34 Å of an interface have thus been observed. We find further evidence that the low-frequency dielectric constant is half the value and the interfacial relaxation time is ~10 times larger in a 34 Å/34 Å superlattice than expected suggesting that the short superlattice wavelength is less than the length scale required to define "bulk" polarization and conductivity.

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The growing expertise in the synthesis of modulated structures has led to a search for modified behavior in numerous properties of superlattices [1]. In this Letter we report one of the first measurements of the low-frequency dielectric response of a superlattice, in this case, the magnetically ordered oxide pair Fe_3O_4/NiO. We find evidence for the interfacial polarization of a superlattice, indicating its highly local electric displacement, and some indication that, in these short-wavelength superlattices, we are probing the fundamental length scale for electrical polarization and conductivity.

Superlattices of Fe_3O_4(magnetite)/NiO have recently been grown using molecular-beam epitaxy (MBE) techniques for the metal constituents in a cyclotron resonant oxygen plasma onto nearly-lattice-matched MgO(001) substrates. The structural, magnetic, and dc electrical transport [2] properties are discussed elsewhere. For the present study, where a plate geometry with conducting electrodes is required, we have used mica covered with a 600-Å Ni electrode followed by the nearly-equal-thickness Fe_3O_4/NiO modulated structure (approximately 34 Å/34 Å with 5000 Å total thickness and 68 Å/68 Å with 8000 Å total thickness) and separate silver paste overlayers for the electrodes. The Ni base layer leads to a preferred (111) orientation of the modulated structure whose observable x-ray sidebands extend to third order. Persuasive evidence of the chemical and structural modulation in this case was obtained from the measurement of the superlattice dc electrical conductivity anisotropy (found to be among the largest known) from which it could be inferred that the conductivity was spatially modulated by at least 6 orders of magnitude for the 34 Å/34 Å superlattice [2].

Complex permittivity data were obtained from impedance measurements of the pure constituent (Fe_3O_4 and NiO) and superlattice (34 Å/34 Å and 68 Å/68 Å) films with the measurement currents perpendicular to the interfaces driven by electric fields ~50 V/cm. Measurements were made on a total of eight samples, two for each, and represented error within 10% for each pair. Figure 1 shows the real parts of the relative dielectric constants $K_r = \epsilon_r/\epsilon_0$ and the dissipation factors (DF) at frequency $f(=\omega/2\pi) = 10^6$ Hz from 20 to 250 K for 5000-Å-thick films of the Fe_3O_4 and NiO constituents (alone) when made in the manner identical to that of their superlattice. Fe_3O_4 shows a major feature in dissipation at 110 K which is the Verwey (metal to insulator on cooling) transition temperature T_V. As expected for a phase transformation, the temperature of this peak remains unchanged (within 2 K) for measurement frequencies from 10^4 to 10^6 Hz. The dissipation peak near 50 K does shift with frequency, however, and in rough ac-

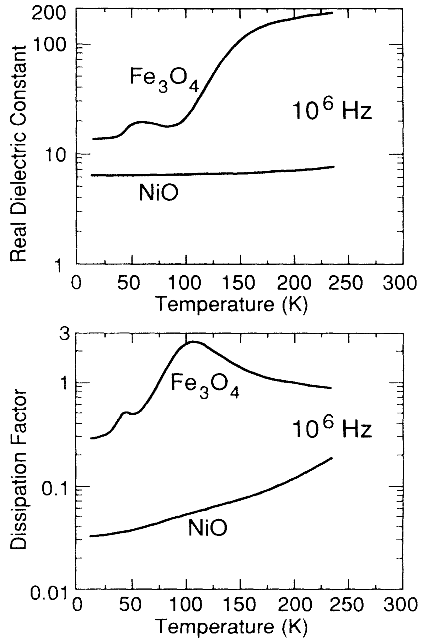

FIG. 1. Relative real dielectric constant (upper) and dissipation factor (lower) vs temperature at 10^6 Hz for films of Fe_3O_4 and NiO. Between 300 and 900 data points were taken over the temperature interval shown, and these have been replaced with a continuous line.

cordance with a relaxation process having an activation energy of ~50 meV as previously found in the acoustic response by Kamigaki [3]. The low-temperature dielectric constant K_r has a value approximately consistent with that reported by Mizushima *et al.* [4], but increases above T_V (not reported by Mizushima *et al.* [4]) to ferroelectriclike values. For NiO, K_r and DF appear featureless, although when extended to temperatures near 300 K (not shown) a Curie-Weiss-like rise in K_r occurs.

The dissipation factor of the 34 Å/34 Å superlattice at $f=10^5$ and 10^6 Hz is shown in Fig. 2. The most important features of these data are (i) a large frequency-dependent peak (and, therefore, not the Verwey peak) which is not observed in the constituent material films, and (ii) a smaller frequency-dependent peak which corresponds to the small Fe_3O_4 relaxation peak. This latter result is strong evidence that the modulated structure has preserved the pure Fe_3O_4 dielectric behavior even at modulation thicknesses of 34 Å. To discuss the expectations of a superlattice based on the constituent behavior, and the significance of the observed behavior, we now briefly review the Maxwell-Wagner model of interfacial polarization [5].

When an electric field is first applied to an interface of materials with dielectric constants ϵ_1 and ϵ_2 and conductivities σ_1 and σ_2 the equality of the normal components of the displacement field D leads to a ratio of electric fields $E_2/E_1=\epsilon_1/\epsilon_2$. Following a time τ_I during which uniform current flow is established, the normal components of $D=\epsilon E$ become discontinuous by a surface charge density in order that the condition $E_2/E_1=\sigma_1/\sigma_2$, required by uniform current flow, be established. In a modulated structure, this surface charge will be supplied by the mobile charge carriers within each constituent and will alternate in sign at successive interfaces. Its displacement will modify the electrical polarization such that for $\omega\tau_I \ll 1$ there will be added dielectric capacity, while for $\omega\tau_I \gg 1$ this contribution is absent. A loss peak in DF occurs at intermediate $\omega\tau_I$. The peak magnitude of DF is approximately proportional to the square of the change in D across the interface [5], and is thus a direct measure of the modulation of ϵ/σ. The interfacial polarization time is

$$\tau_I = \frac{\tau_2(l_1/\sigma_1)+\tau_1(l_2/\sigma_2)}{(l_1/\sigma_1)+(l_2/\sigma_2)}, \tag{1}$$

where $\tau=\epsilon_r/\sigma=1/\omega\mathrm{DF}$ is the component electrical response time and the l's are the relative thicknesses of the constituent materials. From the data of Fig. 1 we see that it is predominantly the Fe_3O_4 which provides the interface charge and establishes the rough equality $\tau_I \sim \tau$ (Fe_3O_4). We have calculated the complex dielectric response of the Fe_3O_4/NiO superlattice based on the constituent behavior from Fig. 1, the l's (nearly equal) from energy-dispersive x-ray analysis measurements and growth parameters, and full formulas given elsewhere [5]. The results are given in Figs. 2 and 3. It should be kept in mind that decreasing T leads to a rapidly increasing τ_I (due to an exponentially falling σ in both constituents) and, therefore, diminishing interfacial contribution to the electrical polarizability.

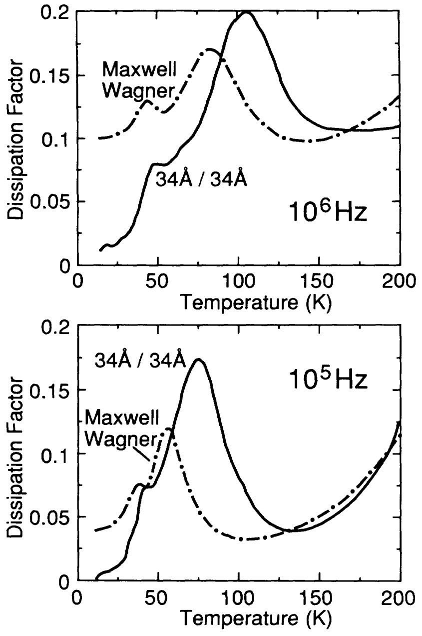

FIG. 2. Observed and calculated (Maxwell-Wagner) dissipation factor vs temperature for a 34 Å/34 Å superlattice of Fe_3O_4/NiO at 10^6 Hz (upper) and 10^5 Hz (lower). Between 300 and 900 data points were taken over the temperature interval shown, and these have been replaced with a continuous line.

The calculated dissipation factors (Fig. 2) show the Maxwell-Wagner ($\omega\tau_I \sim 1$) interfacial polarization peak as the major feature to be expected [6]. Since the major feature of the observed superlattice behavior is not found in the constituents, and is of the relaxation type with

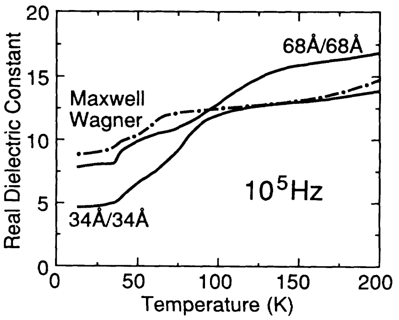

FIG. 3. Observed (34 Å/34 Å and 68 Å/68 Å Fe_3O_4/NiO superlattices) and calculated (Maxwell-Wagner) relative dielectric constants vs temperature at 10^5 Hz. Between 300 and 900 data points were taken over the temperature interval shown, and these have been replaced with a continuous line.

magnitude comparable to that calculated, we take this peak to correspond to interfacial polarization in the superlattice. The shift in temperature (or frequency) between the observed and predicted peaks, however, indicates a large discrepancy between the calculated and actual relaxation times since σ and τ depend exponentially on $1/T$.

One may assume that a source of discrepancy in the calculated behavior can lie in the use of macroscopically determined ϵ's and τ's (from thick films) which would be inappropriate in the superlattice if its wavelength were shorter than that needed to establish, for example, the bulk constitutive relations $D=\epsilon E$ and $J=\sigma E$. Evidence of the latter (only indirect) has been given elsewhere [2]. Some indication of the former may be provided by Fig. 3. The low-temperature dielectric constant (which will be free of relaxation effects since $\tau_I \rightarrow \infty$ as $T \rightarrow 0$) shows that the superlattice with 68 Å/68 Å wavelength has $K_r \rightarrow 9$ ($T \rightarrow 0$), which is not far from the expected (Maxwell-Wagner free) component model value. At half this wavelength, however, the real dielectric constant is substantially smaller, and this may indicate that the process controlling the lost polarizability requires more than 34 Å in spatial extent to be operable.

While these results demonstrate that a fundamental length scale for K_r may have been reached, the numerical discrepancy in K_r is far too small to account for the observed temperatures for the peak dissipation factors in the superlattices. This behavior, therefore, must result from conductivities (and τ's) near interfaces that differ grossly from "bulk" values. Note from Fig. 2 that the predicted Maxwell-Wagner peak at 10^5 Hz occurs at a temperature close to that of the observed peak at 10^6 Hz. Thus, we may roughly [7] estimate $\tau_I(\text{observed}) \sim 10\tau_I(\text{predicted})$ (at 80 K). Since $\tau_I \sim \tau(\mathrm{Fe_3O_4})$, as noted above, we may finally conclude, quite crudely, that the conductivity of Fe_3O_4 within 34 Å of the interface is $\sim \frac{1}{10}$ its bulk value. Though not shown here, the 68 Å/68 Å superlattices exhibit a comparable or greater discrepancy in the position of the dissipation peak, indicating that dimensionality effects remain at this length scale.

While numerical discrepancies have not been accounted for, a simple picture of hydrogenic orbits in these oxide superlattices emerges to explain some unusual transport and dielectric properties and to provide a relevant length scale for their existence. The temperature dependence of the low-field Fe_3O_4 film electrical conductivity has shown [2] the presence of a thermally activated process with $E_A \sim 50$ meV. The small loss peak in DF and the change in K_r for Fe_3O_4 at ~ 50 K, reported here, correspond to the same E_A and show that the activated conductivity process may contribute to the polarizability as well. Finally, the strong nonlinear current-voltage behavior observed [2] for Fe_3O_4 was related to the Poole-Frenkel effect and implied dielectric constants of ~ 10. Such "impurity" or "mixed valency" orbits with $E_A = 50$ meV and a dielectric constant of ~ 10, which we now see occurs in these Fe_3O_4 films, would lead to Bohr orbits ~ 30 Å in diameter. Furthermore, the prior study of electrical conductivity in the superlattices has also shown that the Poole-Frenkel effect is modified if the (half) modulation wavelength is reduced to $\sim$30–60 Å. If, now, in addition, the polarizability is due in part to these orbits (as might be expected for "large atoms"), then the relevant length scale for the dielectric response, as well as the transport behavior, is one or two Bohr orbit diameters $\sim$30–60 Å. This will again exceed the available space in a short-wavelength superlattice and cause the dielectric response to be modified from its bulk behavior. Such models would seemingly also lead to nonlocalities in the definitions of ϵ and σ near interfaces, thus making a simple adjustment of their values an improper approach in further analysis. Figure 2 clearly shows the central result, however, that unlike lightly doped *p-n* junctions, these superlattices allow large electric displacement modulations over 34 Å.

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[1] See, for example, *Physics, Fabrication and Applications of Multilayer Structures* (Plenum, New York, 1989).

[2] G. Chern, S. D. Berry, D. M. Lind, H. Mathias, and L. R. Testardi, Appl. Phys. Lett. **58**, 2512 (1991), and references therein.

[3] K. Kamigaki, J. Phys. Soc. Jpn. **16**, 1770 (1961).

[4] K. Mizushima, K. Nakai, S. Tanaka, and S. Iida, J. Phys. Soc. Jpn. **44**, 1831 (1978).

[5] For an excellent discussion, see A. R. von Hippel, *Dielectrics and Waves* (Wiley, New York, 1954), pp. 228ff.

[6] Note that, because of interfacial effects and the NiO response, there is little evidence of the Verwey transition in the calculated superlattice dissipation even though it is present in the constituent behavior.

[7] Based on the (only) approximate condition $\omega\tau_I \sim 1$ at the peak dissipation for the Maxwell-Wagner effect in our case. The neglect of NiO in this argument is not well justified.