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Paramagnetism, Antiferromagnetism, and Superconductivity in La_2NiO_4

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ESR and energy loss measurements at 9 GHz have been carried out on granular samples of $La_2NiO_{4.00}$ in the range from 3.8 K to room temperature. The observed phenomena are dependent on the temperature and O_2 sample treatment. For exactly 4.00 oxygen stoichiometry, the ESR spectra indicate that the material undergoes a series of phase transitions which are of some importance for understanding the antiferromagnetic and/or superconducting behavior observed in La_2NiO_4. A low temperature regime ($3.8 < T < 70$ K) is characterized by a zero field microwave absorption signal and by the noise generated in fields above 0.3 T; this is conventionally interpreted as a very sensitive signature for the presence of superconducting domains. There also is a broad, temperature-independent ESR absorption arising from antiferromagnetic domains. Phase transitions are identified by changes in the ESR spectra above 70 and 160 K. Above 160 K (162–298 K), the ESR spectra remain unchanged, as would be expected for the ESR absorption from antiferromagnetic domains (the Néel temperature for La_2NiO_4 has been reported as high as 650 K). The transition near 160 K is interpreted as being due to the onset of motional narrowing of the spin–spin interactions in the crystal.

1. INTRODUCTION

Magnetic response measurements of samples cooled in a nearly zero magnetic field have shown that the susceptibility of some annealed $La_2NiO_{4.00}$ specimens becomes negative below 70 K and decreases with a hyperbolic dependence on temperature to ≈ -0.7 emu/g near 4.2 K (1a). While the majority of the La_2NiO_4 work in the literature identifies the material as antiferromagnetic with a Néel temperature as high as 650 K (1b), microwave measurements have confirmed that in these samples both the ac and the dc resistivity decrease with temperature below $T = 70$ K (1c). On this basis, the authors concluded that a transition to a minority superconducting phase in these materials can occur below 70 K (1). There is a similar change from antiferromagnetic to superconducting behavior as a function of increasing oxygen content in $YBa_2Cu_3O_{7-\delta}$; superconductivity is observed for $\delta < 0.3$ (2). The theoretical interpretation concerning the transition to superconductivity in La_2NiO_4 is based on the similarity of the two types of phase transitions (1a, 3). In this work, we search for supporting evidence for the presence of superconductivity and/or antiferromagnetism in carefully prepared (1a), granular $La_2NiO_{4.00}$ using ESR absorption spectroscopy. The challenge to the chemist then is to ascertain the role that oxygen stoichiometry plays in either type of phase transition. ESR absorption measurements permit the determination of the magnetic state of the samples; the ESR spectrometer also measures the energy loss exhibited by materials in zero field near their superconducting transition temperature T_c; this subject has been reviewed by Adrian and Cowan (4). The technique has been applied in studies of conventional superconductors and of superconducting cuprates, both in single crystal and in granular ceramic materials. Thus, the technique has become a very helpful tool in detecting the step-like decrease in resistance to zero near T_c (1c, 4, 5). The dependence of the superconducting transition temperature on the presence of a magnetic field allows one to distinguish this transition from other nonmagnetic-field-dependent phase changes when field modulation is used (4). Here, measurements of the ESR properties and of those associated with the superconducting transition provide insight on the antiferromagnetic and superconducting properties of $La_2NiO_{4.00}$.

2. EXPERIMENTAL

The samples were prepared as described in the literature (1a). In order to observe any signal related to superconductivity in $La_2NiO_{4+\delta}$, it has been repeatedly found necessary to render δ as close to zero as possible. Accordingly, ground-up single crystals obtained through the use of the skull-melting technique (1e) were maintained under an O_2 fugacity in the range $-11.6 < \log(p/\text{atm}) < -11.4$

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for 2 hr at 1000°C and rapidly quenched to room temperature. CO/CO_2 buffer mixtures were used for the control of O_2 fugacity, which was directly measured by a standard Y_2O_3–ZrO_2 oxygen transfer cell. The ground crystals were placed into 4-mm o.d. ESR quartz tubes under Ar and stored until the time of the measurements, when He was introduced for heat transfer.

The ESR spectra and the energy loss (4, 5) (from an oscillating field $2\mathbf{i}B_1 \cos 2\pi\nu t$, ν = 8 kHz–9 GHz in a modulated external field $(B_z + 2B_{zm} \cos 2\pi\nu_m t)\mathbf{k}$, ν_m = 0.4–10^2 kHz, detected near $B_z = 0 \pm 10$ mT) are shown in Figs. 1 and 2. They were obtained using a Bruker 200 ESR spectrometer with a dual cavity arrangement and an Oxford 900 cryogenic system (6). When lock-in detection is used, the energy loss signal arises from a modulated energy absorption in low fields by a superconductor (the acronyms mealfs (5c) or mamma (4) at 9 GHz are introduced to distinguish this response from standard ESR signals). Sample cooling through the transition temperature (70–60 K) proceeded at a rate of 1°/10 min, as described earlier (1a). A dc field was applied to the sample cavity in order to sweep through $H = 0$; therefore, the abscissa values in Figs. 1 and 2 are 6–7 mT above the actual magnetic field. The field was calibrated by the ESR absorption at 9 GHz and at 8 MHz of a free radical reference 1,1′biphenylene–2phenylallyl, which permits a quantitative analysis to be made (5c, 6). The mealfs signal was recorded every 10° from 60 to 4 K; then the temperature was raised to 60 K and a new cooling cycle was started. Reproducibility was achieved in successive temperature cycles through T_c which were carried out at least twice for each sample. In one case, Sample PM was reannealed in CO/CO_2, as described above, after the first low temperature measurements. The results agreed with the first set of studies. Figures 1 and 2 show the mealfs and ESR data for several samples labeled PM, PMR, and PMR4. The modulation field amplitude was varied in order to obtain the best signal-to-noise ratios. The percent of the total modulation amplitude, MA (0.28 mT peak to peak), is reported on all spectra. The amount of powdered

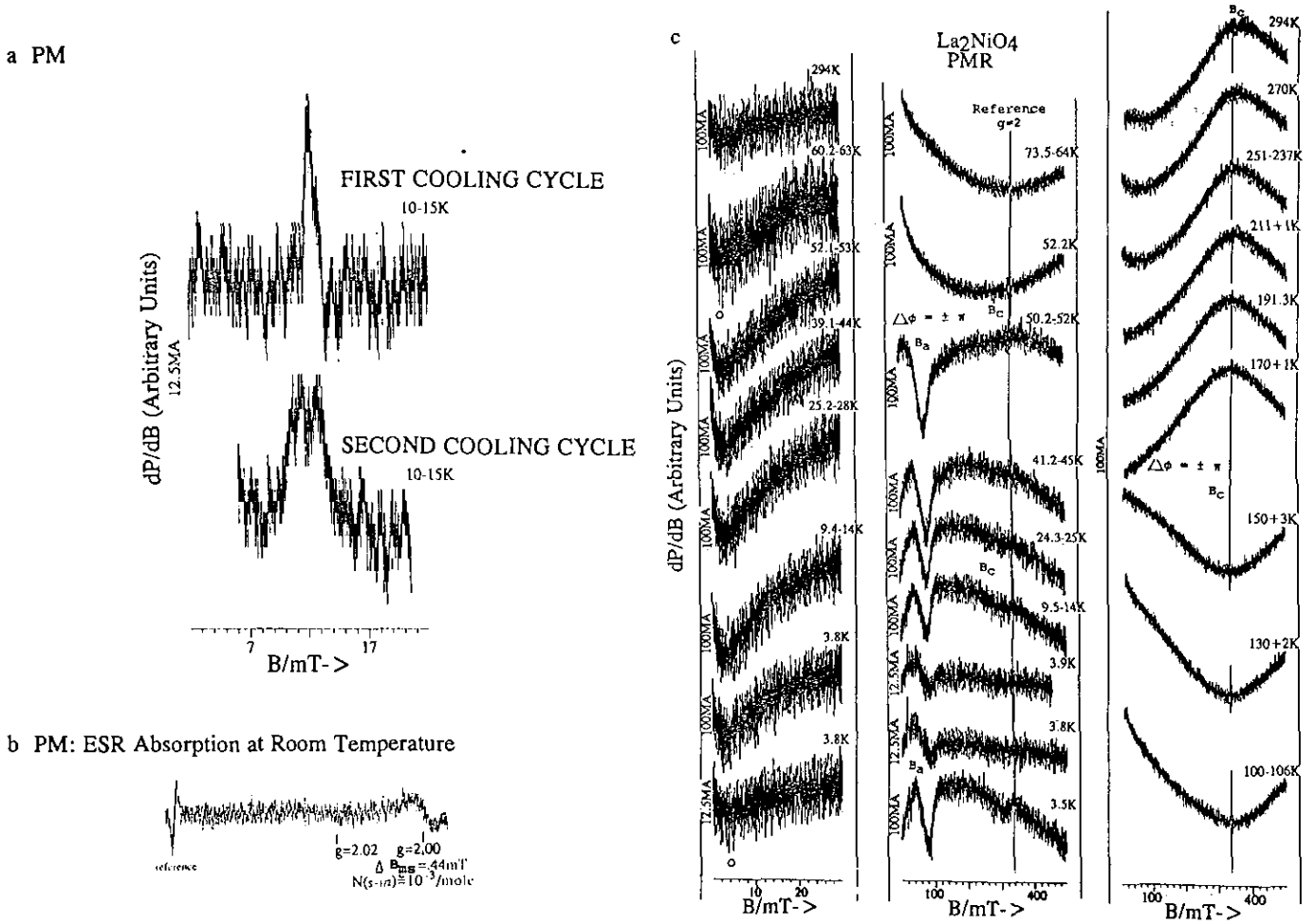

FIG. 1. Microwave spectra of Sample PM/PMR: (a) Sample PM absorption derivative of the microwave energy loss $dP/dB_z \propto di(B)/dB_z$ versus B_z for the first and second cooling cycles. The signal disappears above 60 K. (b) Sample PM ESR absorption derivative (dX''/dB_z) at room temperature near $g = 2$. (c) Microwave spectra for Sample PMR. Different field scans are shown.

sample used (10–100 mg) was determined by the best tuning conditions of the microwave cavity. Out of five samples measured, only one labeled PMR3 produced neither an ESR nor a mealfs response.

A DIANO 800 system was used for the XRD and XRF measurements (Fig. 3).

3. RESULTS: 9 GHZ MEASUREMENTS

The phenomena observed are categorized as follows: in the lowest temperature regime (3.8–70 K), for an oxygen stoichiometry of 4.00, a zero field nonresonant absorption and high magnetic field noise (characteristic of superconductors) are observed, together with a broad antiferromagnetic resonance absorption derivative. Phase transitions are detected through changes in the ESR response for $70 < T < 90$ K and at 162 K. In the temperature regime (162–298 K), the ESR spectra remain unchanged.

Figures 1a and 1b show the mealfs response for Sample PM in the first two cooling cycles and the ESR signals at room temperature. The mealfs signal increases to a maximum between 10 and 15 K. After heating to 60 K and cooling in zero field, the amplitude of the signal in the second cycle is the same as in the first cycle but is twice as broad and vanishes at the center of symmetry (zero field), as predicted by theory when cooling is done in zero field (5b). Sample PM was subjected to higher magnetic fields, up to $B_z = 340$ mT, in order to measure the ESR spectra (Fig. 1b), only after the low temperature measurements were completed. Two room temperature ESR absorptions occurring at $g = 2.00$, $\Delta B_{ms} = 0.44$ mT and at $g = 2.02$ are due to centers present at a concentration of 10^{-3} mole units per mole of La_2NiO_4, assuming $S = \frac{1}{2}$. Sample PM was subsequently reannealed in an O_2 atmosphere ($\log(p/\text{atm}) = -11.5$ at 1000°C (1a, 1e)) and relabeled Sample PMR. The mealfs response for PMR (Fig. 1c) passes through a maximum near 40 K and vanishes above 60 K. The Sample PMR mealfs signals are broader than those for Sample PM, and the ESR absorptions in Fig. 1c exhibit narrow lines only near 3.5 K ($g = 2.00$ and 2.10 and $\Delta B_{ms} < 1$ and 20 mT, respectively). Another signal (near $B_a = 50$–100 mT, $\Delta B_{ms} = 20$ mT) increases to a maximum near 50 K and then vanishes. A second broad magnetic resonance absorption ($B_c \approx 200$ mT ± 100 mT) appears near 9 K, with a metallic Dysonian line shape that changes very little up to room temperature, except for reversible changes by $\pm\pi$ in the sample ESR reference phase above 50 and 160 K. This was observed in two different temperature cycles; it is an indication of discontinuous changes in the sample conductivity.

The spectra for Sample PMR4 ($La_2NiO_{4.00}$, different batch prepared as Sample PM (1a, 1e)) in Fig. 2 are similar to those for PM or PMR in the low temperature regime, $3.8 < T < 70$ K. Figure 2 shows a very weak mealfs signal near 3.8 K which reached a maximum near 21 K and vanished by 34 K. The magnetic resonance spectra above 74 K appear as a complex powder pattern. The broad ESR absorption derivative centered near $B_b \approx 200 \pm 70$ mT is similar to that observed for the PMR specimen. Above 74 K, the broad resonance centered near B_b is replaced by a powder pattern, with the same overall width but with sharp absorption derivative extrema. The overall width of the powder pattern remains the same up to 162 K, where a sharp ESR absorption ($g = 13$, $\Delta B_{ms} \approx 4$ mT) appears and then disappears by 215 K. Above 100 K, the center of gravity of the powder pattern shifts by 50 mT to lower field and then remains unchanged up to room temperature.

4. DISCUSSION OF RESULTS

4.1. *Energy Loss and ESR Measurements*

A review of the generally accepted explanation for a zero field energy loss signal in superconductors has appeared recently (4). This involves the response of a superconductor to an oscillating magnetic field provided by the ESR spectrometer. As the externally applied dc field changes, the flux quantization varies discontinuously (5c). The expression for the current tunneling across a finite Josephson junction is then given by (7)

$$i(\mathbf{B}) = i_{max} \left|\sin(\pi \mathbf{B} \cdot \mathbf{A}_{J,t}/\Phi_0)/(\pi \mathbf{B} \cdot \mathbf{A}_{J,t}/\Phi_0)\right|, \quad [1]$$

where $\Phi_0 \equiv h/2e = 2.067 \times 10^{-15}$ Wb is the quantum unit of flux and $\mathbf{A}_{J,t}$ has the magnitude of the total area of the Josephson junction with the unit vector along the normal direction. Relation [1] follows from the same arguments used to derive, and is equivalent to, the Fraunhofer diffraction relation in optics. It was used early on to explain the fine structure observed in resistivity measurements (7a). In a randomly aligned granular sample, it is not possible to measure the predicted periodicity of $i(\mathbf{B})$. Thus we propose that the mealfs signals in Figs. 1 and 2 are due to the average of the first current oscillation predicted by [1] for a randomly oriented sample; here we follow the averaging procedure by Jeffries *et al.* (5b). Accordingly, if the normal to a junction area $A_{J,t}$ makes an angle θ with the external field, the average over orientations between $\theta = 0$ to $\pi/2$ determines the width between the points of maximum slope in Fig. 2a, $\Delta B_{z,ms}$. This quantity may be compared with relation [1]; i.e.,

$$\langle \Delta B_{z,ms} \cdot A_{J,t} \cdot \cos\theta \rangle \approx 0.5\, \Delta B_{z,ms} \langle A_{J,t} \rangle = 1.3\, \Phi_0. \quad [2]$$

Relation [2] then yields

$$\sqrt{\langle A_{J,t} \rangle} \approx \sqrt{(2.6\, \Phi_0/\Delta B_{z,ms})} \approx 2.2\, \mu\text{m}, \quad [3]$$

which is smaller than the normal metal skin depth. This strongly suggests that the mealfs signal observed for sample PM is due to filamentary superconductivity. The second-cycle signal in Fig. 1a vanishes at exactly zero field. This characteristic was also found and explained by symmetry in superconducting $YBa_2Cu_3O_7$ (5b); it indicates that temperature cycling in a magnetic field produces permanent effects in the magnetic properties of these materials.

The room temperature ESR signal (Fig. 1b) is due to paramagnetic centers at concentrations three orders of magnitude lower than those for centers producing the broad ESR absorption near $B_a < B_b \approx B_c$. Neither the width nor the intensity for the latter changes with T; i.e., the Curie–Weiss law is not satisfied. This suggests that the absorption arises from antiferromagnetic (AF) domains as described by Kittel (7b). In nonconducting materials, far below T_N, sharp resonance absorptions can be induced, with the sublattices precessing collectively; the AF resonance condition for $B_z = 0$ is (7b)

$$(h\nu/g\beta)^2 = B_A(B_A + 2B_E), \qquad [4]$$

where B_E is the exchange field and B_A is the axial field. In uniaxial antiferromagnets $B_A \parallel B_z \neq 0$ is replaced by $B_A \pm B_z$ and [4] leads to

$$(h\nu/g\beta - B_z)^2 = B_A(B_A + 2B_E), \qquad [5]$$

which becomes the normal resonance condition in the absence of AF alignment. The extrema in Figs. 2a,b identify the two resonance fields predicted in [5]. A center resonance is due to nonaligned domains. Then $(B_AB_E)^{1/2} = 131.6$ and 197.2 mT with $g = 10.6$ and 8.1 for the high temperature (HT) at 294 K and low temperature (LT) at 100 K phases, respectively. These values are considerably lower than those for MnF_2 of $B_E = 5.4$ T and $B_A = 880$ mT at 0 K (7b). The LT to HT phase transition near 160 K reduces $(B_AB_E)^{1/2}$, suggesting that there is either motional narrowing of the spin–spin interactions or canting of the spins (7c). The Néel temperature is above 298 K (1).

The similarities in the properties of samples PMR and PMR4 are manifested between 3.8 to 70 K in the microwave response and in the room temperature structure detected by XRD in Fig. 3. However, there are differences between the spectra for PMR and PMR4 above 70 K: the ESR absorption for PMR4 sharpens above 74 K while that for PMR does not. The appearance of the sharp ESR absorptions near 162 K, which disappear by 215 K in Sample PMR4, may be associated with a transition to a semiconducting phase, for which signals with high g values have been observed (8). The metallic Dysonian line shape of the AF resonance in PMR remains unchanged from 9 K to room temperature, but the ESR spectra indicate that the sample undergoes transitions above 50 and 160 K. Thus, the ESR data indicate that $La_2NiO_{4.00}$ undergoes phase transitions above ≈70 and 160 K, independent of whether the sample is metallic (PMR) or semiconducting (PMR4) in antiferromagnetic domains. We do not know the reason for the different metallic/semiconducting behavior above 70 K.

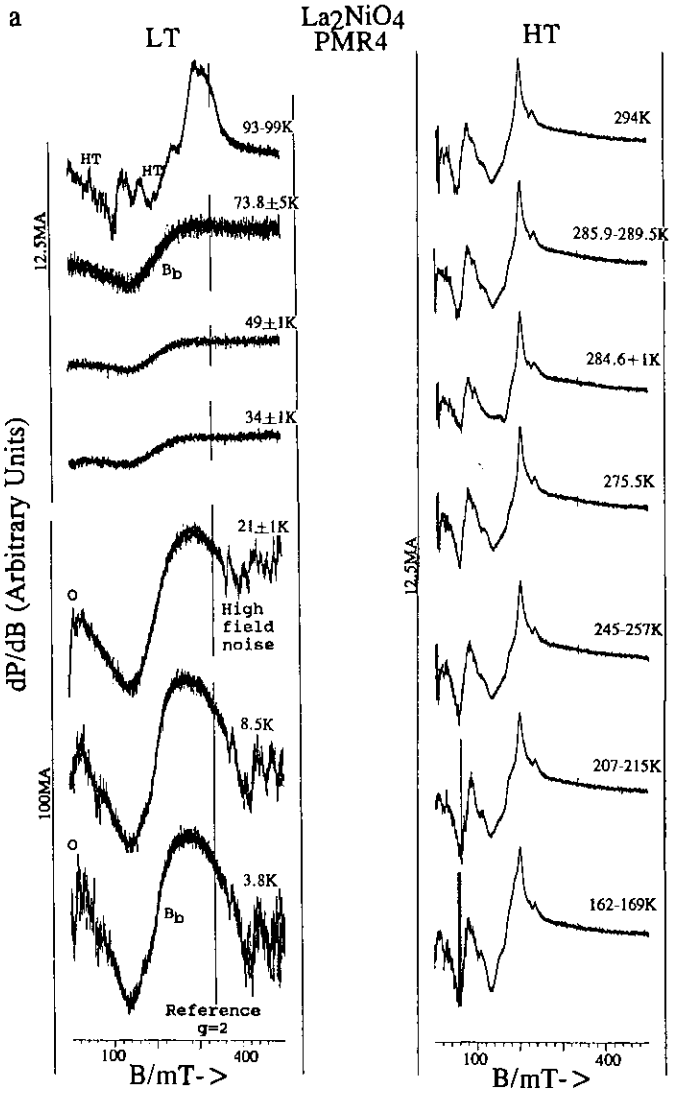

FIG. 2. Microwave spectra of Sample PMR4: absorption derivative of the microwave energy loss dP/dB_z versus B_z. (a) First cooling scan. Noise is detected above $B_z \approx 400$ mT, which can be associated with flux expulsion from 3.8 to 21 K. (b) Second cooling scan.

The above discussion is based on the premise that both antiferromagnetic ordering and superconductivity are being observed in these samples. For the sake of completeness, an alternative explanation should be considered. Near $B_z = 0$, a signal may be observed in ESR spectroscopy when $h\nu$ matches exactly the transition of a high spin state $F = I + S \geq 1$ (9) or when $h\nu$ matches exactly the anisotropy field of one antiferromagnetic domain (7b). The zero field transitions for a high spin state which

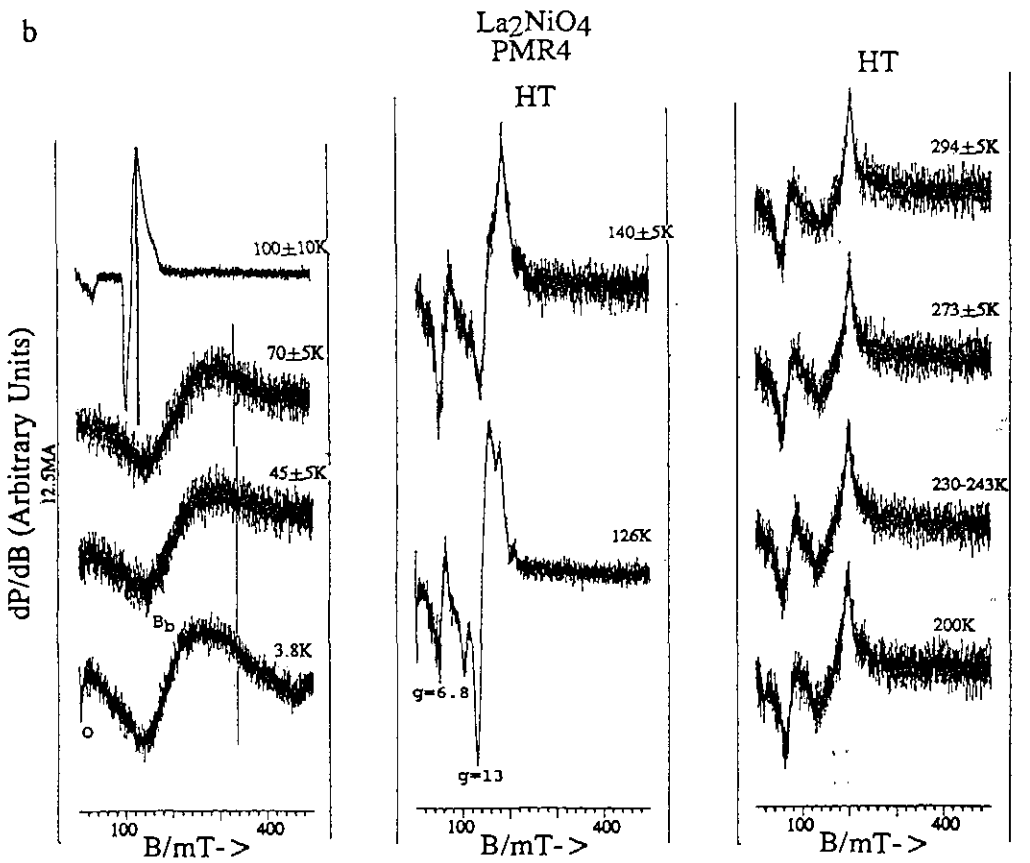

FIG. 3. Comparison of XRD (Cu$K\alpha$) data for Samples PMR and PMR#3.

matches $h\nu$ exactly would have to be reflected in the ESR spectrum. In the range from 3.8 K to room temperature, the zero field signal passes through a maximum before vanishing; therefore, Curie's law is not obeyed. The AF resonance where one axial field fortuitously matches $h\nu$ exactly would have to be of the same intensity as the resonances observed near $B_a < B_b \approx B_c$, unless the resonance is associated with a second antiferromagnetic phase. Neither of these arguments explains the high field noise; therefore, we cannot eliminate the possibility of the presence of superconducting states. In PMR4, the powder pattern is broad in the range where we observe zero field absorption; it narrows only at temperatures above that where the mealfs vanish, suggesting that other states producing the mealfs signal do contribute to the relaxation mechanism and are in dynamic equilibrium with the AF states; e.g.,

$$AF_{states} \rightarrow Other_{states}, \qquad [6]$$

where the first order rate constant, obtained from the AF resonance line width, is $k = 1/T_2 \approx 10^{10}$/sec. The sharpening of the AF resonance absorptions above 70 K must indeed be associated with transitions in the solid which affect a relaxation channel in reaction [6]. The shift in field and the narrowing of the powder pattern above

162 K must be correlated with the onset of motion of crystalline groups since motion averages the spin–spin interaction terms to half of the value observed in the rigid configuration (7b). Near 162 K, the phase transition from pseudotetragonal to orthorhombic most probably destroys the uniaxial symmetry. Evidence for AF resonance has also been obtained for $La_2NiO_{4.00}$ (dispersed in epoxy which was allowed to set in a high magnetic field) by *k*-band microwave absorption with no modulation (1d).

4.2. *Comparison of 9 GHz Results with the XRD and XRF Data*

The XRF and XRD patterns for Samples PMR and PMR4 were checked for consistency with the reported structure and single phase composition. The XRD data (Fig. 3) indicate that the diffraction pattern for Samples PMR and PMR4 exhibit structure in the 006 peak at room temperature. Such structure is absent in samples that do not exhibit mealfs nor ESR response, e.g., in Sample PMR3. The broadening of the 006 diffraction in PMR is similar to the effect of fluorination in La_2NiO_4 (10). Differences in the La L-edge XRF in PMR and PMR4 with respect to a standard La_2O_3 and PMR3 also indicate that La sites are involved in the structural and spectroscopic changes. The intensity of the La : L3 and L2 X-ray edges in $La_2NiO_{4.00}$ are comparable to the Ta L-edges in metallic disulfides TaS_2 and $TaSe_2$ (11). This property has been identified with the 3*d* percentage of the conduction band in the disulfides (11b), indicating that the oxygen stoichiometry may be just one factor in determining the change in the Gibbs free energy for the phase transition to the superconducting and/or antiferromagnetic state.

5. CONCLUSIONS

Mealfs signals and high field noise were observed in four out of five $La_2NiO_{4.00}$ specimens below 70 K. Such signals are conventionally interpreted as a very sensitive signature of superconducting phases near T_c (4). There is a remote possibility that the mealfs signal arises from an antiferromagnetic phase different from that detected near $B_z \approx 200$ mT. The dominating antiferromagnetic resonance signals indicate that there is a competition between the free energy change for the superconducting and antiferromagnetic transitions. This effect is already documented for $YBa_2Cu_3O_{7-\delta}$ (2) and is therefore of great importance for future experimental and theoretical developments in superconductors other than those based on cuprates. We cannot, however, ascertain exactly the small fraction of the sample that is superconducting nor determine whether both paramagnetism and antiferromagnetism coexist with superconductivity, nor whether the two types of states occur in different regions in the samples. However, the relaxation processes, leading to the broadening of the AF resonance when the mealfs signal and the high field noise are present, also suggest that other states (which are associated with this type of response) are in dynamic contact with the antiferromagnetic domains.

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