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Magnetic Properties of Quasi-Two-Dimensional La_2NiO_4

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Magnetic susceptibility studies on single crystals of nearly stoichiometric La_2NiO_4 with the applied field both parallel and perpendicular to the c axis show a transition at 204 K below which two-dimensional canted antiferromagnetic order seems to exist. This oxide also undergoes a transition from isotropic to anisotropic susceptibility near 100 and 250 K.

Introduction

Although K_2NiF_4 has long been known to be a two-dimensional Heisenberg antiferromagnet (*1, 2*), efforts to demonstrate the existence of long-range order in the corresponding oxides of nickel have not met with success (*3–7*). These attempts were based on several early studies of magnetic properties. A small anomaly, manifested as a discontinuity in the slope of the Curie-Weiss law plot for La_2NiO_4, was reported by Smolenskii *et al.* (*4*) and by Ganguly *et al.* (*5–7*), but no evidence of long-range order was observed down to 4 K. As a result of a careful study of the preparation and characterization of single crystals of Ln_2NiO_4 (Ln = La, Pr, Nd) compounds (*8–10*), it became apparent that both the structural and physical properties of these compounds strongly depend on the deviation from ideal oxygen stoichiometry, δ in $La_2NiO_{4+\delta}$, as determined by the Ni^{3+} content. Samples prepared by ceramic procedures or from the melt invariably contain appreciable concentrations of Ni^{3+} (typically 3–15%). La_2NiO_4, which has recently been shown to possess orthorhombic symmetry ($Bmab$–D_{2h}^{18}) (*9, 10*), approaches tetragonal symmetry when the proportion of Ni^{3+} becomes appreciable. Furthermore, any antiferromagnetic order in $La_2NiO_{4+\delta}$ could be suppressed by the ferromagnetic interactions introduced by Ni^{3+} ions. Measurements of magnetic susceptibility between 300 and 800 K on powders of uncertain provenance have also been recently described (*11*).

In this study we report the results of an investigation of the anisotropic magnetic susceptibility of pure single crystals of La_2NiO_4 which are nearly devoid of Ni^{3+}. This study establishes for the first time the presence of long-range quasi-two-dimensional antiferromagnetic order in single-crystalline La_2NiO_4, as well as transitions from isotropic to anisotropic susceptibility near both 100 and 250 K.

Experimental

Large single crystals of 99.99% La_2NiO_4 were prepared by the technique of radiofre-

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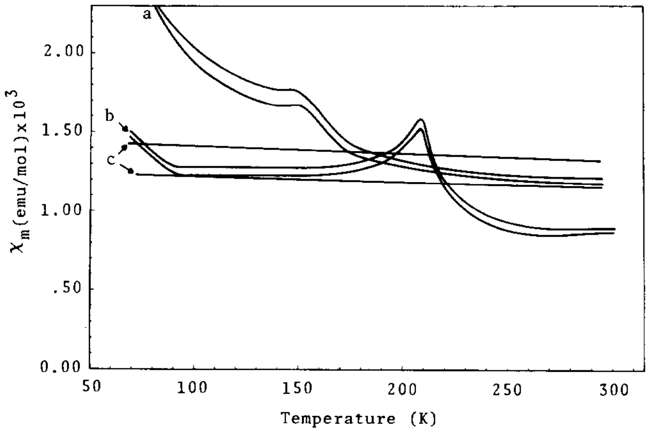

FIG. 1. The variation of susceptibility $\chi_{\parallel}$ with temperature T for three single-crystal $La_2NiO_{4+\delta}$ specimens: (a) unannealed specimen ($\delta \sim 0.1$); (b) sample annealed at 1470 K, $Kf_{O_2} = 4.6$, ($\delta \leq 0.005$); (c) sample annealed at 1470 K, $Kf_{O_2} = 8.5$ ($\delta \sim 0$). Magnetic field aligned with c axis of the K_2NiF_4 structure; upper curve in each set: applied field $H = 5000$ G; lower curve in each set: applied field $H = 6500$ G.

quency skull melting. Details of the crystal growth procedure and subsequent characterization are described elsewhere (*9, 10*). The crystals were found to be single phase by X-ray powder diffraction, polarized reflected light microscopy, and direct lattice imaging.

Single-crystal specimens were oriented, cut, and annealed in flowing CO_2 or CO/CO_2 gaseous buffers at 1470 K in a horizontal furnace for 1 week, followed by rapid quenching. The Ni^{3+} content of the annealed samples was below the limit of detection by iodometric titration under nitrogen; $[Ni^{3+}] < 0.5\%$. To avoid possible reoxidation, the exposure of samples to air was minimized after annealing.

An automated Faraday balance was employed for measurement of magnetic susceptibility. The applied field was generated by a Varian V-4005 4 in. electromagnet equipped with constant-force pole caps. Specimens (~50 mg) were contained in a 60-mg quartz bucket suspended by means of a fine tungsten wire from a Cahn Model RG electrobalance. The field gradient was calibrated using $CoHg(SCN)_4$ as a standard. Variable temperature operation was implemented with an Alfa Model 3013 temperature controller and a non-inductively wound heater. Sample orientation in the applied field was visually verified from above the balance. Corrections were applied to compensate for the effect of the bucket and for the underlying diamagnetic susceptibility ($\chi_{dia} = -1.00 \times 10^{-4}$ emu/mole) of La_2NiO_4.

Results and Discussion

At the outset one should note that as $\delta \rightarrow 0$ the magnetic susceptibility χ of $La_2NiO_{4+\delta}$ becomes almost temperature independent. This is brought out in Fig. 1, which presents the T dependence of $\chi_{\parallel}$, the magnetic susceptibility of single crystals with the applied magnetic field, $\mathscr{H}$, directed along the c axis of the K_2NiF_4 structure. Data were taken on unannealed specimens ($\delta \sim 0.05$), and on specimens annealed under oxygen fugacities f_{O_2} for which $-\log f_{O_2} \equiv Kf_{O_2} = 4.6$ ($\delta \sim 0.0025$) and $Kf_{O_2} = 8.5$ ($\delta \rightarrow 0$). The changeover with decreasing δ from a strong temperature-dependent susceptibility to an essentially constant susceptibility is clearly in evidence. An anomalous peak is found for the two specimens whose composition deviates from the ideal La_2NiO_4 stoichiometry. Similar trends were observed for orientation-averaged magnetic susceptibilities measured on $La_2NiO_{4+\delta}$ powders for which $\delta = 0.097$, 0.060, and 0.015 (*12*). As anticipated, the susceptibility is somewhat dependent on the applied magnetic field.

In what follows we concentrate largely on susceptibility studies of specimens for which the Ni^{3+} concentration is estimated to be approximately 0.5 at.% of the total Ni content. It is this latter specimen that exhibited the most pronounced magnetic susceptibility anisotropy. The drop of $\chi_{\parallel}$ with rising T was intermediate between specimens which showed a pronounced decrease in $\chi_{\parallel}$ ($\delta \sim 0.05$) and samples with essentially no change of $\chi_{\parallel}$ ($\delta \rightarrow 0$).

Plots of the temperature variation of the magnetic susceptibility $\chi_{\parallel}$ and $\chi_{\perp}$ measured parallel and perpendicular to the c axis of the specimen annealed at $Kf_{O_2} = 4.6$ are shown in Figs. 2a and b, respectively. The difference, $\Delta\chi \equiv \chi_{\parallel} - \chi_{\perp}$ is plotted against temperature in Fig. 2c, and the derivative, $d\Delta\chi/dT$, obtained from a detailed study near the transition, is presented in Fig. 2d. The shape of the parallel susceptibility curve, with a sharp cusp, clearly indicates the onset of magnetic order; there also exists a weak ferromagnetic moment along c, as determined by the torque on the sample in the applied field. The transition temperature, determined from the maximum in the derivative of the susceptibility (Fig. 2d), was found to be 204 K. The small variations of χ with applied magnetic field are again consistent with magnetic ordering in the temperature range below ~250 K.

Nearest-neighbor NiO_6 octahedra are tilted in opposite directions away from the c axis in the (001) plane of the orthorhombically distorted La_2NiO_4 structure (*10, 13*). The observation of a weak net ferromagnetic moment along c suggests that La_2NiO_4 is a canted antiferromagnet. The tilting of octahedra removes the inversion symmetry which would otherwise be present between nearest-neighbor Ni sites in the undistorted structure, thereby permitting spin canting, as a manifestation of the Dzialoshinskii-Moriya antisymmetric superexchange interaction (*14, 15*).

The anisotropy in susceptibility shown in Fig. 2 is rather atypical for standard 2D materials in that it extends over the temperature range 100–250 K; outside the above temperature interval La_2NiO_4 acts magnetically as a nearly isotropic material. In the present case the magnetic anisotropy extends to rather higher temperatures ($100 \leq T \leq 250$ K) than for most other layer-type compounds. The nature of the transition to isotropic susceptibility at 100 K is at this point not understood; however, it is interesting to note that a modified Curie-Weiss law extends down to at least 65 K. The isotropy at temperatures beyond 250 K is in line with the general finding (*2*) that short-range order may persist to temperatures well above the Neél point in layered materials.

The parallel susceptibility of an unannealed La_2NiO_4 crystal containing approximately 10% Ni^{3+}, plotted against temperature in Fig. 1, shows a much broader, attenuated, local maximum in the susceptibility near 155 K than the sharp cusp observed in the sample containing 0.5% Ni^{3+}. This is consistent with the minimal octahedral distortion present in such grossly nonstoichiometric samples. Previous studies of the magnetic behavior of La_2NiO_4 have involved either unannealed specimens (*3–6, 8*) or annealed crystals which were ground and exposed to air for extended periods prior to measurement (*7, 8*). The absence of evidence for long range order in these cases might be attributed to the use of nonstoichiometric polycrystalline samples. It is not clear why a previous neutron diffrac-

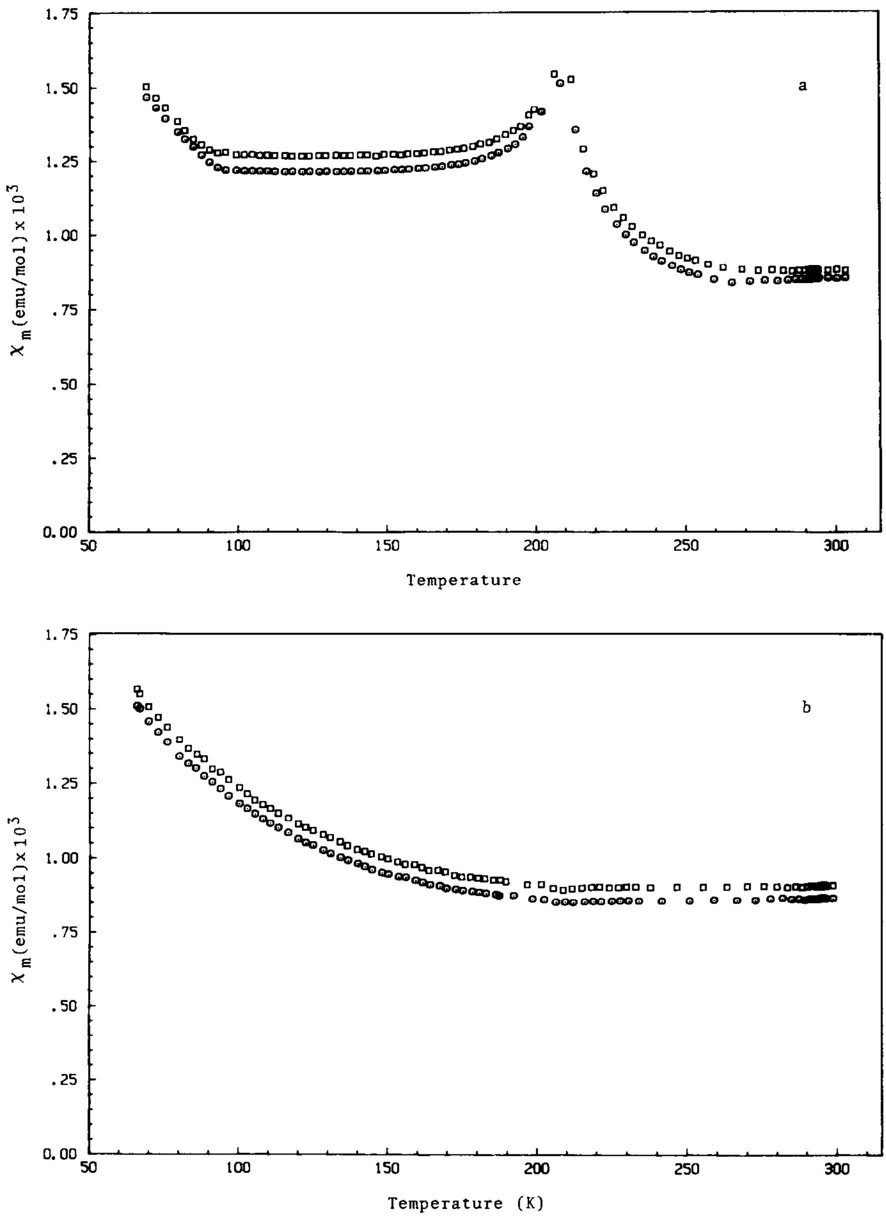

FIG. 2. (a) Plot of magnetic susceptibility vs temperature for a single crystal of La_2NiO_4 annealed at $\log f_{O_2} = -4.6$ and 1470 K. Magnetic field oriented along the c axis. Various sets of experimental points correspond to different applied magnetic fields. Top curve, H = 5000 G; bottom curve, H = 6500 G. (b) Same type of plot as Fig. 2a. Magnetic field oriented within basal plane. (c) Difference curve between Figs. 2a and b. (d) Derivative of curve shown in Fig. 2c.

tion study revealed no evidence of long-range order (*16*).

It should be noted that, as shown in Fig. 2 for the annealed specimen with Kf_{O_2} = 4.6, the quantity $\chi_{\parallel} = 1.3 \times 10^{-3}$ emu/mole is virtually independent of temperature be-

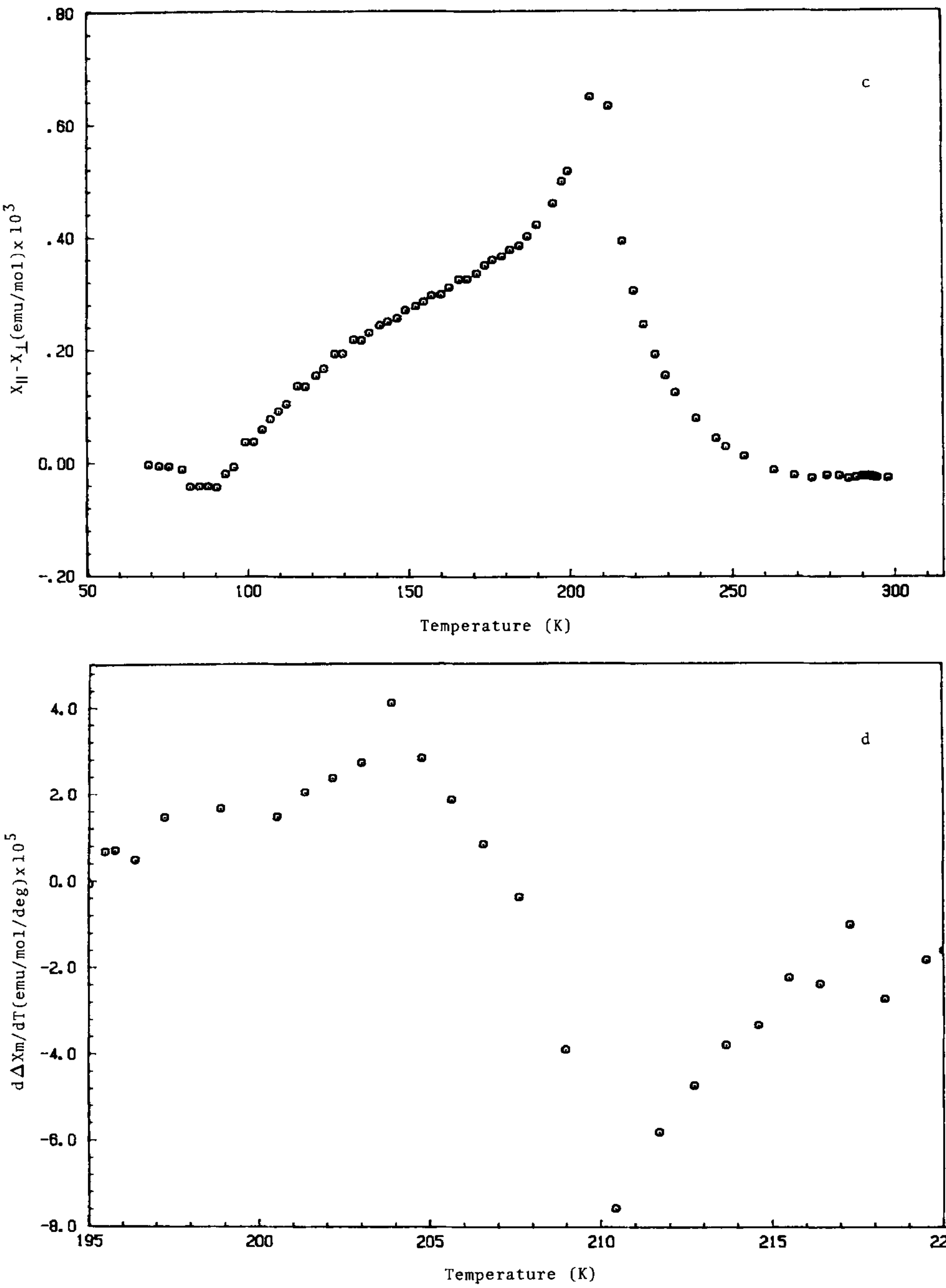

FIG. 2—*Continued.*

tween 100 and 180 K; $\chi_{\perp} = 0.85 \times 10^{-3}$ emu/mole is essentially constant over the range 210–475 K, and $\chi_{\parallel}$ assumes the same limiting value beyond 250 K. These observations for annealed single crystals of La_2NiO_4 are reflected to a lesser degree in

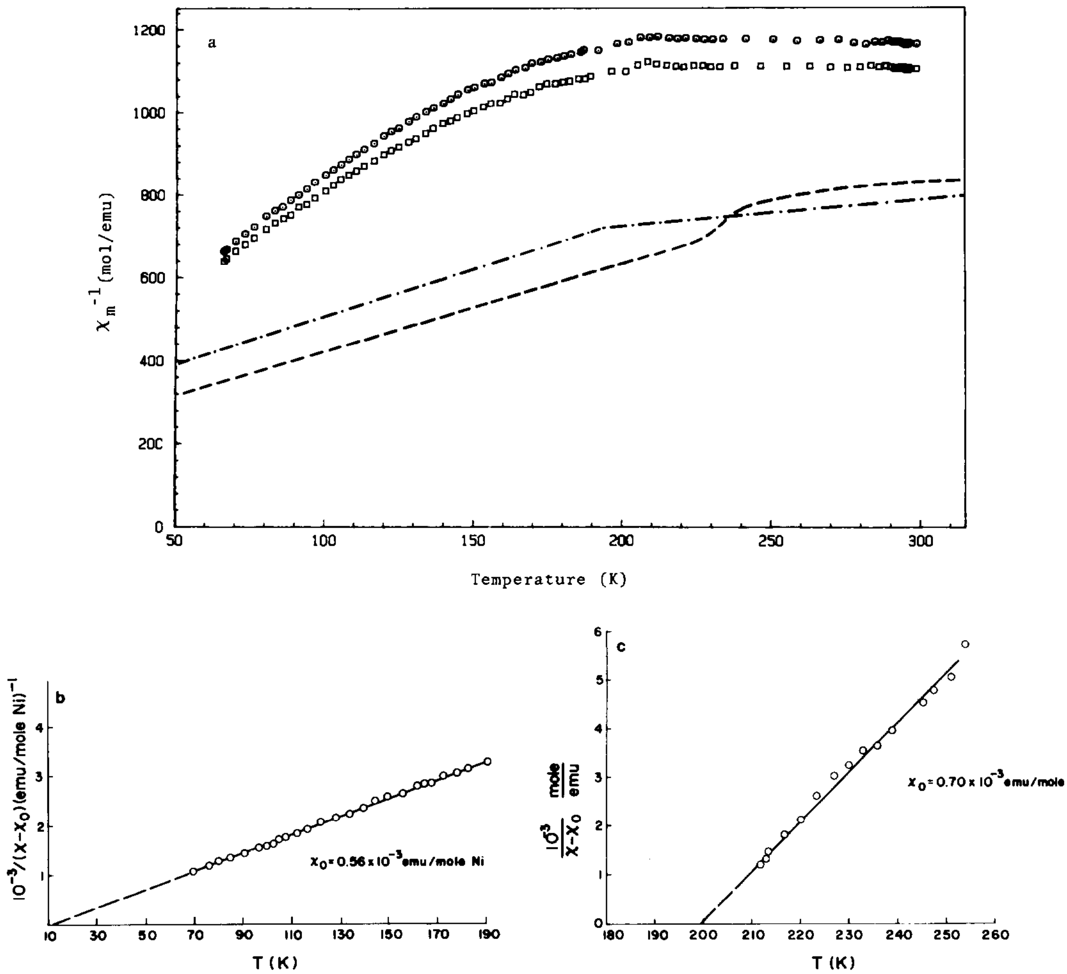

FIG. 3. (a) Experimental points: Curie-Weiss plot for experimental data displayed in Fig. 2a. Dashed curve: data cited in Ref. (*5*); dot-dashed curves: data cited in Refs. (*6*) and (*7*). (b) Plot of experimental data of Fig. 2a to test the modified Curie-Weiss law $\chi = \chi_0 + C/(T - \theta)$. (c) Modified Curie-Weiss law as applied to the data of Fig. 2b beyond 204 K.

unannealed specimens (see Fig. 1). The parallel susceptibility of nearly stoichiometric La_2NiO_4 ($Kf_{O_2} = 8.5$) was essentially constant ($\chi_{\parallel} = 1.5 \times 10^{-3}$ emu/mole) from 80 to 400 K and then started to rise with temperature. The various transitions show a very slight dependence on applied field, with the higher fields producing a lower transition temperature.

An attempt was made to fit the data of Fig. 2b to a Curie-Weiss law. Figure 3a demonstrates that resulting plots of χ_M^{-1} vs T deviate from the anticipated straight line above 110 K. Data reported in prior work (*5–7*) are entered as dashed and dot-dash lines. The data shown in Ref. (*8*) vary considerably, depending on the provenance and thermal history of the samples, but show roughly the same trend as those in Refs. (*5–7*). It is evident that the susceptibilities $\chi_{\perp}$ as determined in the present measurements lie well below the orientation-

TABLE I

PARAMETERS USED IN THE ANALYSIS OF SUSCEPTIBILITY DATA ACCORDING TO THE CURIE-WEISS LAW[a]

	Reference	Temperature range (K)	$\chi_0 \times 10^3$ emu/mole	em θ	C $\left(\frac{\text{emu-K}}{\text{mole}}\right)$	μ_{eff} (μ_B)	S
1	6,7	200–300	0	−500	1.15	3.03	1.1
2	6,7	4–190	0	−117	0.42	1.83	0.54
3	5	300–700	0	−400	0.82	2.56	0.87
4	5	4–190	0	−68	0.375	1.72	0.51
5	Present work	67–110	0	−55	0.180	1.22	0.29 ($S_\perp$)
6	Present work	67–190	0.56	+13 ($\theta_\perp$)	5.40×10^{-2}	0.432	0.098 ($S_\perp$)
7	Present work	200–270	0.70	+199 ($\theta_\parallel$)	1×10^{-2}	0.282	0.02 ($S_\parallel$)

[a] $\chi = \chi_0 + C/(T - \theta)$; $C \equiv \mu_{eff}^2 N_A/3k$; $\mu_{eff} \equiv \sqrt{4S(S+1)}\ \mu_B$. N_A is Avogadro's number, k is Boltzmann's constant, S is the spin, μ_B is the Bohr magneton.

averaged values reported by other investigators. Correspondingly, the various parameters θ, C, μ_{eff}, S (ordering temperature, Curie constant, effective magnetic moment in Bohr magnetons, and spin) of Refs. (*5–7*) are considerably larger than the corresponding quantities deduced from Fig. 3a. All of these quantities are entered in lines 1–5 of Table I. It should be noted that the ranges of validity of the Curie-Weiss law are also much larger in the earlier as compared to the present work. In particular, where we encounter an essentially temperature-independent susceptibility between 250 and 475 K, the earlier workers noted a variation of χ with T which follows the Curie-Weiss law. Finally, one should note that all θ values obtained in these various analyses are negative.

Clearly, the application of the conventional Curie-Weiss expression to the data of Fig. 2a is suspect because of the rather limited range of temperature over which these data could be fit. Accordingly, we attempted to apply a revised version of the type $\chi = \chi_0 + C/(T - \theta)$, wherein χ_0 is a temperature-independent molar susceptibility; this may arise from Van Vleck paramagnetism or from the coexistence of two sets of charge carriers in a very narrow band and a somewhat broader band (*17*), as described below. As Fig. 3b shows, for $\chi_0 = 0.56 \times 10^{-3}$ emu/mole a plot of $(\chi_\perp - \chi_0)^{-1}$ vs T yields a good straight line over the entire temperature range 67–190 K in which $\chi_\perp$ exhibits a temperature dependence. The corresponding parameters are entered in line 6 of Table I. These particular quantities lie in the ranges comparable to those cited by Mohan Ram *et al.* (*18*) in their analysis of magnetic properties of the $LaSr_{1-x}Ba_xNiO_4$ system.

It was also deemed of interest to attempt a fit of the $\chi_\parallel$ data beyond the peak of the curve of Fig. 2b to the same Curie-Weiss law as $\chi_\perp$. Figure 3c shows that the quality of the fit was not as good as that of Fig. 3b, but an adequate representation of the data was achieved with the parameters shown in line 7 of Table I; the temperature-indepen-

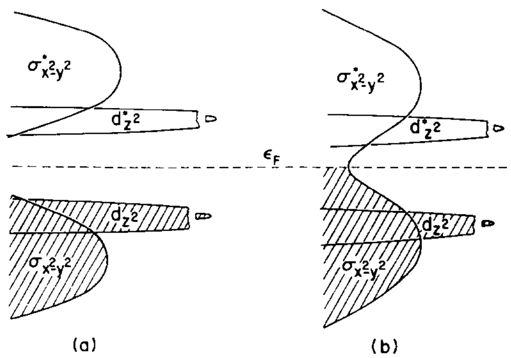

FIG. 4. Proposed resolved density-of-states (DOS) curves for bands near the Fermi level in La_2NiO_4. The d_{z^2} and $d^*_{z^2}$ bonding and antibonding states form narrow bands whose orbital lobes are directed along the c axis. The $\sigma_{x^2-y^2}$ and $\sigma^*_{x^2-y^2}$ states arise from $d_{x^2-y^2}$ orbitals whose lobes lie in the basal plane. (a) DOS for $T \lesssim 650$ K; (b) DOS for $T \gtrsim 650$ K.

dent susceptibility is given by $\chi_0 = 0.70 \times 10^{-3}$ emu/mole.

Discussion

The analysis of data as reported in lines 1–5 and 7 of Table I involves ordering temperatures which are numerically comparable to or even larger than the temperatures over which the measurements were taken. Standard curve fitting of the measurements with $\chi_0 = 0$ yielded effective moments that correspond to 1 to 2 unpaired electron spins for the nickel cation in La_2NiO_4. The present fit with the correction for χ_0 leads to much smaller values of spin. One should particularly note the fact that the analysis invoking the modified Curie-Weiss law now leads to positive Weiss temperatures.

Measurements taken with the applied magnetic field perpendicular to the basal plane yield a small ordering temperature of $\theta_\perp = 13$ K and a spin $S_\perp = 0.1$, both of which signal the existence of a small ferromagnetic spin component along the c axis; presumably this is due to a slight canting of the antiferromagnetically aligned spins away from the basal plane.

A similar analysis of the $\chi_\parallel$ data ($\delta \sim 0.0025$) in the 200–270 K temperature range yields a very small spin $S_\parallel = 0.02$ and a *formal* ordering temperature of $\theta_\parallel = 199$ K. This value coincides almost exactly with the transition temperature of 204 K as read off from Fig. 1d. However, it must be recognized that this formal analysis of the $\chi_\parallel$ data must still be put on firmer grounds by a fundamental interpretation of the interactions in the basal plane. Additional physical measurements would be extremely helpful; unfortunately, prior neutron diffraction studies down to 4.2 K (*16*) and Mössbauer investigations by the Goodenough group (*19*) were carried out on specimens of oxygen stoichiometry quite different from that of the present study, so that these findings are not directly applicable to the current series of experiments.

A band-structure diagram that may be developed on the basis of conductivity studies is shown in Fig. 4. As documented elsewhere (*8, 10*), nearly stoichiometric La_2NiO_4 exhibits semiconducting properties for electron transport within the basal planes of the distorted K_2NiF_4 type structure. The conductivity is characterized by an activation energy of $\varepsilon_\sigma \approx 0.05$–$0.07$ eV, a value which is only of the order of a few multiples of kT. The corresponding mobility activation energy is estimated to be $\varepsilon_u = 0.02$–0.04 eV (*10*), essentially comparable to kT. The conductivity along the orthogonal c direction is associated with nearly the same activation energies but is up to three orders of magnitude smaller than the conductivity along the basal plane.

The resulting density-of-states diagram displayed in Fig. 4, is a revised version of a diagram postulated by Goodenough and Ramasesha (*17*). The left part deals with the temperature range of the present measurements: a gap $\varepsilon_g \sim 0.06$ eV separates the largely filled bands from a largely empty set. Here the d_{z^2} and $d^*_{z^2}$ density-of-states peaks represent extremely narrow bonding and antibonding bands, analogous to Hubbard subbands, derived from orbitals weakly overlapping along the *c* axis; the wider $\sigma_{x^2-y^2}$ and $\sigma^*_{x^2-y^2}$ bands are formed from overlaps of $d_{x^2-y^2}$ orbitals along the basal plane. The situation shown on the right prevails above ~650 K, where La_2NiO_4 undergoes a semiconductor-metal transition for current flow in the basal plane, whereas no transition is encountered along the orthogonal direction (*8*).

The band diagram of Fig. 4 constructed on the basis of mobility studies also rationalizes the magnetization properties described above. In particular, the diagram furnishes a description of the coexistence of essentially localized electrons (along the *c* axis) with nearly free electrons (within the basal plane) that is consistent with the sizeable χ_0 values. The itinerant electrons in the $\sigma_{x^2-y^2}$ band are presumably responsible for the canted antiferromagnetism below the ordering temperature $\theta_\perp = 204$ K. The Curie-Weiss law $C/(T - \theta)$ appears to be due to the nearly localized electrons d_{z^2} electrons which are only weakly coupled to the spins of the $\sigma_{x^2-y^2}$ electrons and which remain paramagnetic to very low temperatures. Moreover, many Ni compounds exhibit large temperature-independent susceptibilities (*20*) due to the presence of closely spaced excited energy levels that yield a large contribution to the standard Van Vleck formulation for χ_0. The small positive $\theta_\parallel$ is reasonable since intra-atomic exchange interactions between d_{z^2} and $\sigma_{x^2-y^2}$-type electrons are weak and ferromagnetic in character.

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