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BRIEF COMMUNICATIONS

Crystal Structure and Semiconductor-Metal Transition of the Quasi-Two-Dimensional Transition Metal Oxide, La_2NiO_4

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Introduction

Crystal chemical considerations (*1, 2*) indicate that among the ternary transition metal oxides of the type A_2BO_4, only La_2NiO_4 should be stable in the K_2NiF_4 structure (*3*). Here, the antiferromagnetic interactions between transition metal ions are essentially confined to the perovskite units in the basal plane. The crystal structure of La_2NiO_4 is indeed reported to be tetragonal (*4, 5*) with the space group *I4/mmm*, whereas both Pr_2NiO_4 and Nd_2NiO_4 are monoclinically distorted (*6*). La_2NiO_4 does not exhibit long-range antiferromagnetic order, but only deviations from the Curie–Weiss law, due to short range interactions (*7*). La_2NiO_4 has been reported to undergo a gradual semiconductor-metal transition near 500 K without any apparent structural change (*8*). The models proposed (*9, 10*) for this transition were based on electrical measurements using pressed pellets of polycrystalline material. We therefore attempted to grow single crystals of La_2NiO_4 and to carry out several types of systematic investigations, with special emphasis on the anisotropic properties of this compound.

Experimental

Single crystal boules of La_2NiO_4 were grown in air by the skull melting technique described elsewhere (*11*). La_2NiO_4 powder was first prepared by the solid–solid reaction of anhydrous 99.99% La_2O_3 (dried in air at 1300 K for 24 hr and cooled under vacuum) and 99.999% NiO (corrected for nonstoichiometry) at 1470 K for 48 hr. X-ray powder diffraction patterns were recorded with a Philips diffractometer, while electron diffraction patterns and lattice images were obtained with a JEOL 200 CX electron microscope. Differential scanning calorimetry was carried out using a Perkin–Elmer DSC-2 instrument. ESR spectra were recorded on a Varian E-109 spectrometer. Magnetic susceptibility measurements were made on polycrystalline samples in the range 10–300 K, using a Faraday balance equipped with a Displex closed cycle cooling system. Four-probe electrical resistivity measurements were carried out with periodic reversal of current direction, using suitably oriented crystals. The extent of oxygen nonstoichiometry was determined by iodometric titration of Ni^{3+} under a nitrogen atmosphere, and confirmed by detection of Ni^{3+} in esr measurements.

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The La/Ni ratio, determined by atomic absorption analysis was 2.00 ± 0.01. High resolution electron microscopic investigation showed no evidence of intergrowth of La_2NiO_4 with $La_3Ni_2O_7$ or higher homologs (*12*).

Results and Discussion

X-ray diffraction patterns of La_2NiO_4 as grown in the skull melter could be indexed on the basis of a tetragonal cell (a = 3.88 Å, c = 12.64 Å) and are similar to those of the ceramic material. However, electron diffraction patterns of the as-grown (unannealed) materials exhibited superlattice reflections corresponding to a $\sqrt{2}$ a type of unit cell (Fig. 1a). Of the Ni, 9.5–11% was determined to be in the trivalent state. Ceramic material with a Ni^{3+} content of 3–5% also exhibited similar superlattice spots in electron diffraction patterns. The superlattice may arise from the distortion of the NiO_6 octahedra or of La–O–Ni angles. We have also noticed such superlattice reflections in Nd_2NiO_4, La_2CuO_4, and La_2CoO_4, all of which form distorted K_2NiF_4 structures.

Annealing of the skull-melted samples in 100% CO_2 at 1470 K for 48–72 hr followed by rapid quenching reduced the Ni^{3+} content below the detection limit (less than 0.5%) and increased the intensity of the electron diffraction superlattice spots. X-ray powder data showed splittings of various reflections, characteristic of a monoclinic unit cell with a = 3.88 Å, b = 3.89 Å, c = 12.52 Å, and γ = 90.37 Å. The ceramic sample produced a very similar X-ray pattern after annealing in CO_2: All samples annealed in CO_2 were found rapidly to acquire excess oxygen when exposed to air.

The superlattice reflections in the electron diffraction patterns of La_2NiO_4 are similar to those encountered in antiferromagnetically ordered K_2NiF_4 (*13, 14*). We suggest that these reflections are intrinsic to the structure and not due to defect ordering. Since La_2NiO_4 is close to the stability limit of the K_2NiF_4 structure, the Ni–O–Ni distance may be somewhat too large for stabilization of the tetragonal K_2NiF_4 structure. Bending of the Ni–O–Ni angle from 180° could be achieved by tilting of the octahedra away from the c axis, or by rotation of the octahedra along the c axis, thus generating a monoclinic distortion of the unit cell. The presence of the smaller Ni^{3+} apparently stabilizes the tetragonal K_2NiF_4 configuration. The new structural features discussed above are incompatible with the reported structure and space group

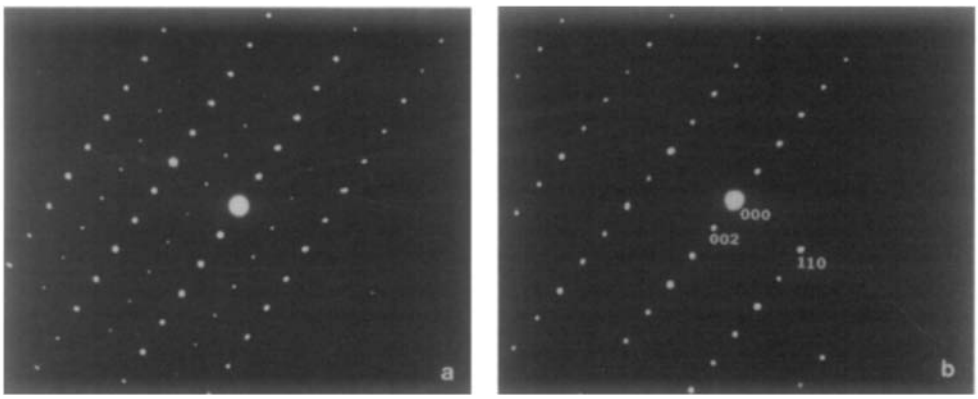

FIG. 1. Electron diffraction patterns of a La_2NiO_4 crystal: (1) 300 K, (b) 400 K.

I4/mmm. The superlattice spots disappear when unannealed samples are heated above 400 K (Fig. 1b). However, no evidence for a structural transition up to 600 K is encountered in DSC scans; thus, any structural and enthalpy changes associated with any transition are likely to be small.

Electron spin resonance spectra show a broad resonance in the temperature range 250–450 K. With increasing temperature the g factor associated with the Ni^{3+} resonance in unannealed specimens decreases from 4.0 to 2.5. Below 250 K the resonance is no longer observed, perhaps due to the onset of short range antiferromagnetic order.

Representative data for the resistivity ρ are shown as a function of increasing temperature T in Fig. 2 for samples annealed in 100% CO_2 and for unannealed specimens. The most striking feature is the occurrence of a resistivity anomaly near 500 K with current flow confined to the basal plane, which is absent when current is directed along the ⟨001⟩ direction. This anomaly is characterized by a change from semiconducting to quasi-metallic behavior; above 550 K a very large positive coefficient of temperature is observed. This transition is not retraced on cooling, but rather follows a higher resistivity path which is dependent on the maximum temperature at which the cooling was commenced. This irreversibility may be due to effects of strain, crystal distortion, charge density waves, or nonstoichiometry. Further investigation of this phenomenon is in progress.

Magnetic susceptibility (χ) measurements for both ceramic and single crystal specimens are summarized in Fig. 3. The results are similar to those reported earlier (*7*) except for an unusual minimum in the

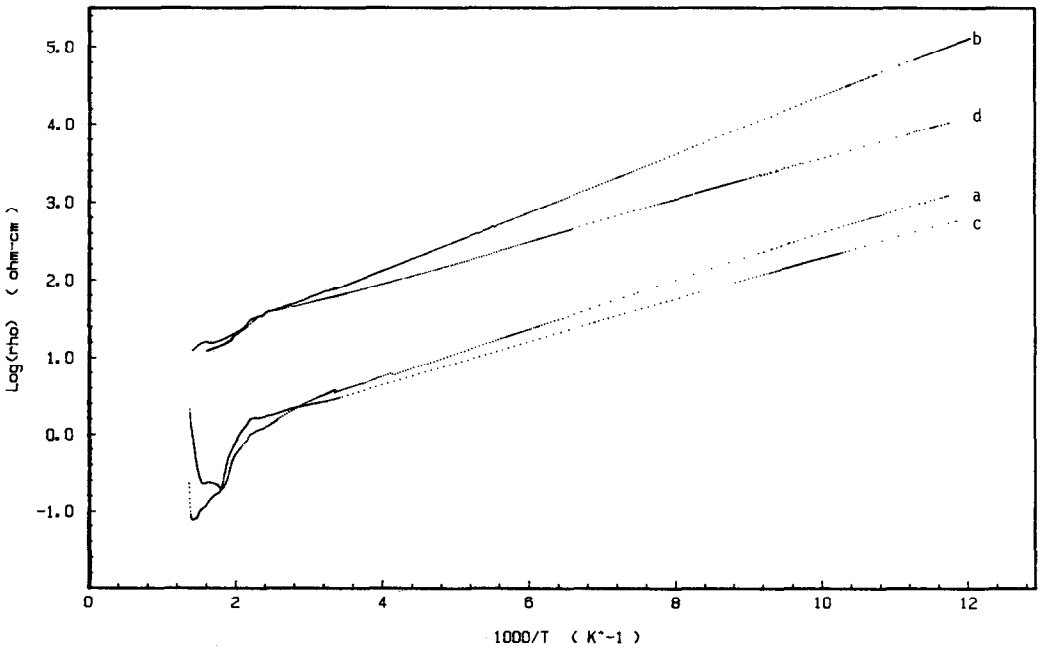

FIG. 2. Resistivity versus temperature for La_2NiO_4 crystals (heating only): (a) as grown by skull melting in air, current directed in the basal plane (ε_σ = 0.061 eV); (b) as (a) with current flow along ⟨001⟩ (ε_σ = 0.074 eV); (c) grown by skull melting and annealed at 1470 K for 125 hr in CO_2, current directed in the basal plane; (ε_σ = 0.054 eV); (d) as (c), current flow along ⟨001⟩ (ε_σ = 0.052 eV).

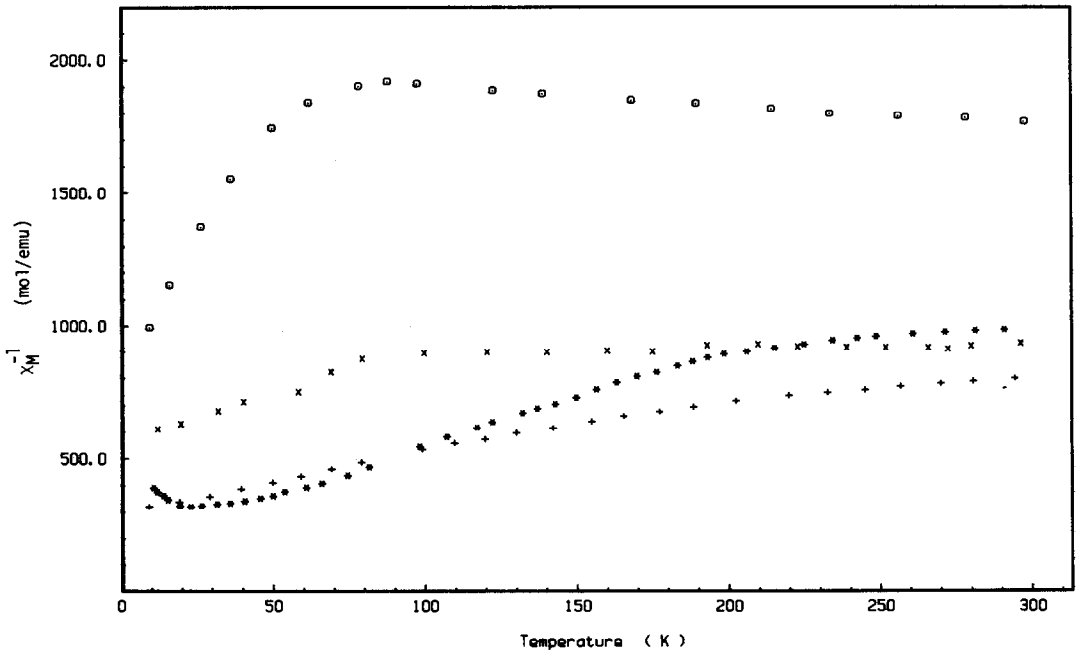

FIG. 3. Magnetic susceptibility results for La_2NiO_4 specimens: (+) air sintered ceramic sample; (*) same as (+) annealed in CO_2 at 1470 K for 24 hr.; (O) ground sample for material skull melted in air; (×) same as (O), annealed in CO_2 at 1470 K for 24 hr.

χ^{-1} vs T plot for the sample grown in the skull melter.

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