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LETTERS TO THE EDITOR

Superconductivity and Antiferromagnetism in $La_{2-x}Sr_xNiO_4$

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We report the observation of superconductivity in $La_{2-x}Sr_xNiO_4$, with transition temperatures up to 70 K, depending on thermal cycling conditions. The existence of superconducting properties in a sample with $x = 0.2$ tests the nature of exchange-mediated pairing since Ni^{2+} ions in these compounds likely are in the spin $S = 1$ state. A coexistence of antiferromagnetism and superconductivity is observed below 20 K and may be due to a structural phase separation at temperatures below 70 K. © 1989 Academic Press, Inc.

Introduction

The striking similarity between $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Sr_xNiO_4$, with respect to both their structure (orthorhombic, K_2NiF_4-type) and their magnetic properties (antiferromagnetism), raises the question of whether the latter compound can be rendered superconducting. If so, the applicability of the current theories of exchange-mediated superconductivity (for recent reviews see (*1*)) would be tested since the Ni^{2+} ion is primarily in the high-spin $S = 1$ state. Furthermore, the relative ease with which large single crystals can be grown (*2*) makes it possible to carry out measurements of anisotropic properties for this quasi-two-dimensional compound in the superconducting state and to consider applications requiring bulk superconductors. We report here on evidence that $La_{2-x}Sr_xNiO_4$ does undergo a transition to the superconducting state, but that great care must be exercised in the sample treatment to achieve this newly observed state.

Experimental Details

Single crystals of $La_{2-x}Sr_xNiO_{4+\delta}$ were grown by a skull melting technique detailed elsewhere (*2*). Specimens roughly $0.5 \times 0.5 \times 0.3$ cm^3 in dimension were oriented, cut into cubic shapes, and annealed at 1000°C under controlled oxygen fugacity, using CO/CO_2 mixtures monitored by an oxygen transfer cell (*3, 4*). The samples were quenched and the exterior portions were trimmed off to achieve a uniform δ value close to zero. The sample was placed in a vibrating sample magnetometer with provision for adjustment of sample temperatures between 2.5 and 300 K. The specimen could be rotated so that either the **c** axis

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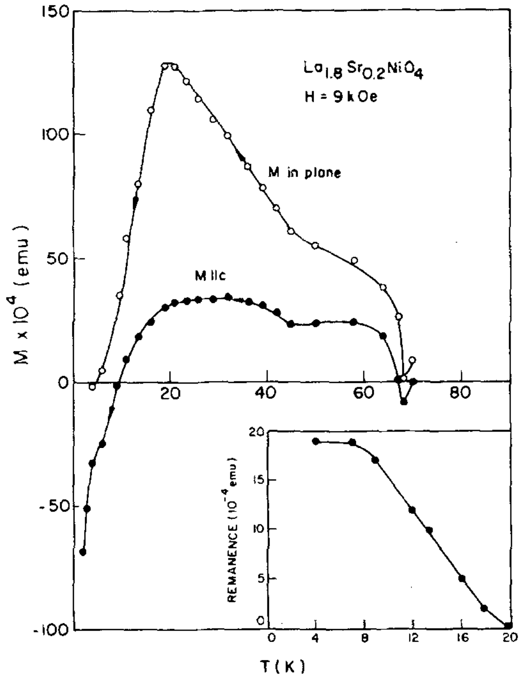

FIG. 1. The temperature dependence of the magnetic moment of $La_{1.8}Sr_{0.2}NiO_4$ during the cooling cycle for an applied field **H** ∥ **c** (lower curve) and **H** ⊥ **c** (upper curve). Note the onset of diamagnetism in the range 63–67 K and below 10 K. The inset shows the in-plane component of the remanent magnetic moment at temperatures below 20 K.

(the long axis of the unit cell) or the ⟨110⟩-type axis in the perpendicular plane could be aligned with applied magnetic fields **H** of up to 15 kOe. Because of twinning it was impossible to distinguish between the **a** and **b** axes in the orthorhombic phase. Four-probe electrical resistivity measurements were carried out in zero magnetic field.

Results

It is stressed at the outset that the results are highly dependent on the history of the thermal cycling of the specimens. The evidence presented later indicates that below 70 K the lanthanum nickelate samples consist of two phases, one of which orders magnetically below 18 K and the other of which becomes superconducting. The observed magnetization therefore depends strongly on the relative fraction of each phase which changes with repeated thermal cyclings.

Figure 1 displays the variation of the magnetic moment M with temperature T in a second cooling run for a $La_{2-x}Sr_xNiO_4$ sample with $x = 0.2$; it had first been cooled slowly from room temperature to 4.2 K and was then reheated slowly to about 75 K, before again being cooled slowly while the indicated magnetization measurements were taken. The top and bottom curves represent results obtained with the applied magnetic field **H** oriented in the plane or along the **c** axis, respectively. The enormous anisotropy of the magnetic moments should be noted. Whereas no diamagnetic signals were encountered in the first run, a very weak negative moment was seen in the second run between 67 and 70 K, and sizeable diamagnetism reappeared below 10 K for **H** ∥ **c**. An extremely weak negative signal was also found at 4.2 K for **H** oriented in the plane. The insert in Fig. 1 shows the remanent in-plane magnetic moment of the sample in the temperature range below 20 K, where the $M(T)$ curve rises with T. These remanence effects, and the 20 K maximum for the in-plane component of the moment, signal the onset of magnetic ordering effects in the plane. Magnetic moment measurements under these conditions also exhibited magnetic aftereffects. Neither remanence nor magnetic aftereffects were encountered when **H** was aligned with the **c** axis or above 20 K with **H** in the plane.

The variation of the magnetic moment with increasing temperature is shown in Fig. 2 for the same specimen in a later run with **H** ∥ **c** = 9 kOe. Here the sign reversal of M was reached at $T = T_c = 24$ K. In still another run the magnetic moment measurements indicated a value of $T_c = 70 \pm 5$ K for

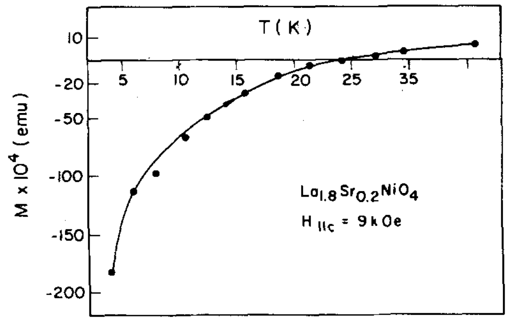

FIG. 2. Magnetic moment of $La_{1.8}Sr_{0.2}NiO_4$ observed when heating the sample. The diamagnetic signal changes sign at $T \simeq 24$ K.

H ∥ **c** and $T_c = 64 \pm 5$ K for **H** in the plane. In this run a very large diamagnetic moment was reached, as shown in Fig. 3, where M is plotted vs **H** at $T = 4.2$ K. The linearity of the data is striking; from the observed slope one calculates a susceptibility $X \approx -10^{-3}$ emu/cm^3, which is roughly 1% of the value $(-\frac{1}{4}\pi)$ for complete flux expulsion from a superconductor. This value is at least two orders of magnitude larger than that for classical diamagnetic systems. The critical field value $\mathbf{H}_{c1}$ exceeds the maximum available applied field of 15 kOe, a magnitude much larger than that of the corresponding cuprates. This feature may be of interest in potential applications. We ascribe the onset of the diamagnetism to the occurrence of superconductivity in a limited portion of the $La_{1.8}Sr_{0.2}NiO_4$ system. A weak diamagnetic moment was also observed below 7 K for a $La_2NiO_{4+\delta}$ specimen with $\delta \simeq 0$. The dependence of M on **H** was not completely linear for runs showing lower values of T_c.

To verify our assertion that the system with $x = 0.2$ undergoes a superconducting transition we performed preliminary resistivity (ρ) measurements with diminishing T in the range 300 to 4.2 K. The data plotted as log ρ vs $1/T$ showed semiconducting behavior at higher temperatures, with an activation energy of $E_a \simeq 0.02$ eV. Beginning at roughly 40 K there is a crossover from semiconducting to superconducting properties with an onset temperature of 19 K.

It is important to note that superconductivity disappears completely after many heating and cooling cycles. However, this property can be recovered by subsequent reannealing at 1000°C for several hours under a properly controlled oxygen fugacity.

Discussion

The simplest interpretation of the above results is based on a model in which $La_{2-x}Sr_xNiO_4$ splits into a two-phase system at $T_c \simeq 70$ K. One of the phases is paramagnetic in the range 70–20 K; below that temperature this phase exhibits substantial in-plane magnetic correlations, in the form of a slightly canted antiferromagnetism. The canting of the magnetic moments leads to the observed remanence and magnetic aftereffects. This particular phase is always present. The other phase is superconducting and grows during thermal cycling at the expense of the magnetic one. The division into magnetic and supercon-

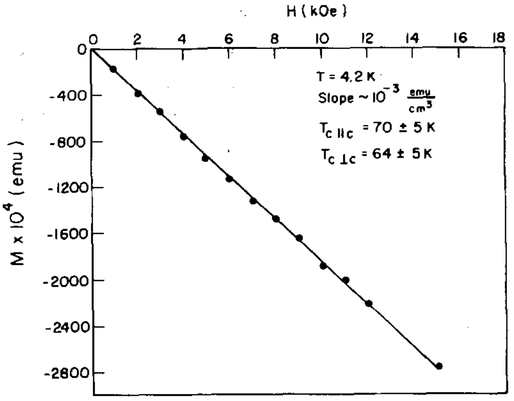

FIG. 3. The dependence of the diamagnetic moment of $La_{1.8}Sr_{0.2}NiO_4$ on applied fields $\mathbf{H} \leq 15$ kOe at $T = 4.2$ K. The susceptibility is roughly 1% of the value $(-\frac{1}{4}\pi)$ for complete flux expulsion.

ducting parts is most probably accompanied by a structural phase separation at about 70 K. Such a separation into two orthorhombic phases has been recently observed (*5*) in $La_2CuO_{4+\delta}$ compounds. The hysteretic behavior of the phase separation induces an uncontrollable subdivision into superconducting and magnetic portions. The onset of diamagnetism therefore occurs at a temperature determined by the mutual compensation of the paramagnetic and diamagnetic components. The highest observed superconducting transition temperature was approximately 70 K, roughly twice as large as that for the corresponding copper compounds. Likewise, pure La_2NiO_4 (*6*) has a Néel temperature of T_N = 650 K, twice as high as that of pure La_2CuO_4 (*7*). Thus, both the experimental data suggesting the relation $T_c \sim T_N$ and the close connection between magnetism and superconductivity strongly indicate a common origin for both transitions.

In the theory of exchange-mediated superconductivity the antiferromagnetic exchange interactions give rise to spin-singlet pairing of electrons. Three such types of pairing have been invoked: *d–d* pairing induced by kinetic exchange (superexchange) (*8*), *p–d* pairing induced by Kondo-type interactions (*9*), and *p–p* pairing (*10*). The last two channels are accessible only if itinerant holes exist in the oxygen *p* band. It can be shown (*11*) that hybridization between O2*p* and Ni3*d* states leads (in fourth order) to antiferromagnetic interactions characterized by the corresponding exchange integrals J_{dd}, J_{dp}, and $J_{pp} \simeq J_{dd}$ (*11*). For the cuprates the relative admixtures of each type of pairing are yet to be determined because the Cu^{2+} ion in the $S = \frac{1}{2}$ state is mixed with the oxygen hole state of the same spin. However, the possible choices for constructing singlet Cooper pairs in the nickelates is far more limited, as discussed below.

It is assumed that Ni^{2+} is in the ground state configuration $S = 1$. The $S = 1$ state corresponds to the aligned two-electron configuration for which Hund's rule holds. Then, a superconducting pairing of neighboring sets of 3*d* electrons would require the formation of a four-electron, spin-paired entity. The motion of such a unit through the crystal would necessitate highly unlikely valence fluctuations involving Ni^{4+} states. Alternatively, if one of the *d* electrons is in a quasilocalized d_{z^2} bonding orbital and the second is in an extended $d_{x^2-y^2}$ bonding orbital, then the motion of the itinerant *d–d* pairs could not take place without violating Hund's rule. Furthermore, *d–p* pairing is unlikely since this involves two *d* electrons with $S = 1$ and a 2*p* hole with $s = \frac{1}{2}$; the motion of such an object would again require a Ni^{4+} valence state; additionally, such a unit is not in a spin-singlet state. We therefore propose that the Cooper pairs are predominantly composed of two *O2p* holes forming a spin singlet. This pairing is mediated by the *p–p* part of the kinetic exchange which originates from virtual $d^82p \rightarrow d^9L$ processes, where *L* represents a ligand state with an additional hole. These virtual *p–d* transitions also lead to Kondo-type interactions which further enhance the kinetic exchange (*p–p*) part (*9*). In such circumstances the superconducting state would be of the BCS type, with a gap anisotropy governed by the ratio of the in-plane and orthogonal exchange integrals. A more detailed discussion of these points will be provided separately.

Conceivably, superconductivity and antiferromagnetism can coexist as a single phase in $La_{2-x}Sr_xNiO_4$; these two states may be associated with the O2*p* and Ni3*d* electrons, respectively. As long as the coherence length for pairing greatly exceeds the wavelength of the 3*d* spin moment periodicity the *p–d* exchange field does not break up the pairs. However, such a single-phase model cannot readily be reconciled with the observed irreversibilities of the thermal cycling processes. Obviously, careful structural studies are needed to settle this problem.

Conclusions

We have observed superconductivity in the $La_{2-x}Sr_xNiO_4$ system with transition temperatures in the range 9 to 70 K, depending on thermal cycling conditions. Below 20 K there are pronounced concurrent magnetic fluctuations which lead to a maximum for the in-plane component of the magnetic susceptibility at $T \simeq 20$ K. The coexistence of superconductivity and antiferromagnetism had been reported earlier in the $La_2CuO_{4-\delta}$ system (*12*) and was subsequently attributed to a separation of the samples into two orthorhombic phases (*5*), of which one was superconducting and the other was antiferromagnetic. The presence of these two phases in our samples is interpreted in terms of a similar structural phase separation which takes place at $T \simeq 70$ K. The singlet pairing of holes of predominantly 2*p* character is believed to be responsible for superconductivity in this system if Hund's rule is obeyed for the Ni3*d* states with $S = 1$.

The above research obviously should be followed up by a careful search for conditions that stabilize the superconducting state of $La_{2-x}Sr_xNiO_4$.

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