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Effects of Ni-to-Cu substitution on the properties of the high-T_c superconductor $La_{1.85}Sr_{0.15}CuO_{4-y}$

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We report experimental data about the influence of Ni substitution on the properties of the high-T_c superconductor $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$, $0 \leq x \leq 0.05$. Superconductivity is totally suppressed above $x = 0.04$ and the Curie law observed at $x = 0.05$ reveals an effective magnetic moment of $0.7\mu_B$ instead of $\sqrt{3}\mu_B$ as for spin $\frac{1}{2}$. This result is explained by the existence of a singly occupied and localized $Ni(d_{z^2})$ level. Possibilities for non-s-wave superconductivity are also discussed in conjunction with our experimental data.

After the discovery of superconducting ceramics giving rise to superconductivity in the range of 36–38 K [for the La-Sr(Ba)-Cu-O series][1] much research effort has been devoted to the understanding of the mechanism which is at the origin of the superconductivity in this class of oxide materials. Structural work and band-structure calculations performed on these oxides suggest that the current is carried by electrons delocalized in a conduction band based on Cu(3d) and O(2p) atomic wave functions.[2] Moreover, the superconducting oxides display a structure belonging to a broader class of materials whose prototype is the two-dimensional antiferromagnetic K_2NiF_4.[3,4] La_2NiO_4 also belongs to the same family.[5] Hence, substitution of Ni for Cu in La_2CuO_4 is expected to be structurally relatively easy.

The critical temperature for superconductivity in the series of $La_{2-x}Sr_xCuO_{4-y}$ is known to be greatly affected by the position of the Fermi level in the conduction band with an optimum condition for T_c when $x \approx 0.15$.[6,7]

In the present work we have studied the effect of nickel substitution for copper on the magnetic and transport properties of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$, $0 \leq x \leq 0.05$. Our data show that the rather modest depression of T_c, which is observed upon Ni substitution, can be understood by the pair-breaking effect of spin-$\frac{1}{2}$ moments coming from singly occupied d_{z^2} levels of nickel ions.

The polycrystalline materials $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$ ($0 \leq x \leq 0.05$) were prepared by nitrate decomposition: $La(NO_3)_3.6H_2O$, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$, and $Sr(NO_3)_2$. Each one is dissolved in water (pH is adjusted to 2); then they are mixed together for 1 h. Flash decomposition is obtained by sudden introduction at 700 °C in a furnance equipped with a strong ventilation system, where samples were held 2 or 3 h. The powder is then disagglomerated by ball milling (with ZrO_2 balls) in isopropyl alcohol, and reacted at 1000 °C under oxygen current. Sometimes, several cycles of calcination and grinding were performed. Note that, after mixing in isopropyl alcohol solution, we obtained particle sizes between 0.2–2 μm (centered on 0.8 μm), as measured with a HORIBA 700 granulometer. Last, the powder is isostatically compressed at 480 MPa, and sintered at 1100 °C. By x-ray diffraction using Cu $K\alpha$ radiation we have monitored the presence of a single tetragonal phase. The crystalline parameters were estimated using 20 peaks of the diffraction spectrum. The final result reported in Fig. 1 is an average obtained by the least-squares method. The precision is typically $\pm 3\text{-}5 \times 10^{-3}$ Å.

Figure 1 shows the tetragonal lattice parameters a and c determined from x-ray diffraction, plotted against the Ni content (%). There is a slight increase in a($\approx$0.1%)

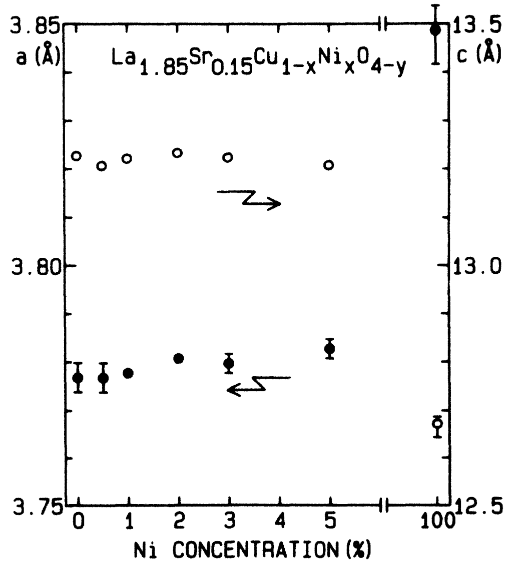

FIG. 1. Variation of the lattice parameters in the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$ system as a function of Ni content (%).

and a very slight decrease in c ($\approx 0.05\%$) with the Ni substitution up to 5% even if they are still far from those of $La_{2-x}Sr_xNiO_{4-y}$.[8,9] The tetragonal structure at room temperature is preserved in spite of Ni substitution.

The resistivity measurements are performed by the standard four-probe method with a low-frequency technique. The current and voltage leads are made of fine gold wires attached to the samples by silver paste. The resistivity data between room temperature and liquid-helium temperature are given in Fig. 2(a). The $x=0$ data agree quite well with the previously published results.[10] The resistivity retains a clear metallic behavior ($d\rho/dT > 0$) down to the superconducting transition temperature. This can be taken as an indication for the good quality of the samples. However, as soon as Ni is substituted for Cu a small resistivity minimum develops and the conduction electrons show a tendency towards localization at low temperature. This localization behavior increases quickly with the amount of the Ni substitution and is accompanied by a decrease of T_c. At 5% substitution there is no superconducting transition down to 4.2 K. Figure 2(b) shows in more detail the temperature dependence of resistance normalized to the 50 K value for various Ni-substitution levels.

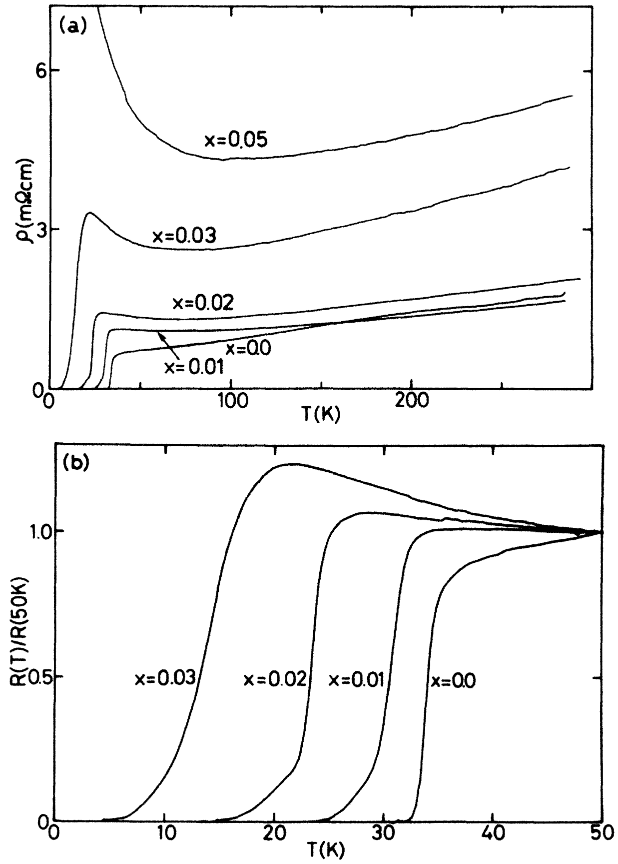

FIG. 2. (a) Temperature dependence of the electrical resistivity of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$. (b) Normalized resistance of the same samples below 50 K.

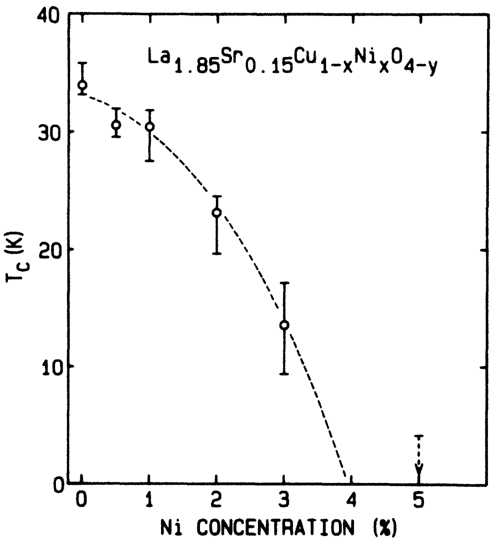

FIG. 3. Ni-concentration dependence of the superconductivity transition temperature. The vertical bars represent the 10–90% transition width.

The extrapolation of the same data on Fig. 3 shows that superconductivity no longer exists in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$ above a substitution level of about $x=0.04$. This dependence of T_c on Ni substitution is more pronounced than that observed in the $YBa_2Cu_3O_{7-\delta}$ series since in the latter compound the only effect of a 17% substitution by nickel is to depress T_c from 92 to 52.3 K.[11]

The magnetic susceptibility of the samples is measured with a superconducting quantum interference device magnetometer in the temperature range 4.2–400 K and in magnetic fields from 50 to 50000 Oe. The lower-temperature results, which represent the superconductivity transition, are displayed in Fig. 4(a) and clearly show the disappearance of the superconductivity with the increase of Ni concentration. All these measurements were performed in the field of 100 Oe except for the $x=0.005$ sample where a field of 50 Oe was used. The data in Fig. 4(a) show that the amplitude of the Meissner expulsion decreases significantly upon substitution. As far as $x=0.03$ is concerned the Meissner expulsion at 6.5 K is about 10^{-3} the value obtained in samples with a lower substitution level [see the inset of Fig. 4(a)].

Shown in Figs. 4(b) and 4(c) are the higher-temperature susceptibility data for the same samples under 10000 Oe except for $x=0.05$ which is under 1000 Oe. The evolution of the temperature dependence with Ni concentration is clear. In $x=0.0$ and $x=0.01$ samples, $d\chi/dT$ is positive at all temperatures. Such a strange behavior of the susceptibility is not clearly understood yet and is opposite to the observations for $YBa_2Cu_3O_{7-\delta}$ where the susceptibility can be fitted very well by a Curie-Weiss law.[12] At $x=0.02$, a small upturn of the susceptibility appears around 55 K and at $x=0.03$ there is no more superconducting transition in this field although $d\chi/dT > 0$ is always verified at higher temperatures. This is not until $x=0.05$ that the susceptibility follows the Curie-Weiss law [Fig. 4(c)] with an effective moment carried by Ni ions of $0.7\mu_B$. This latter value is indeed much

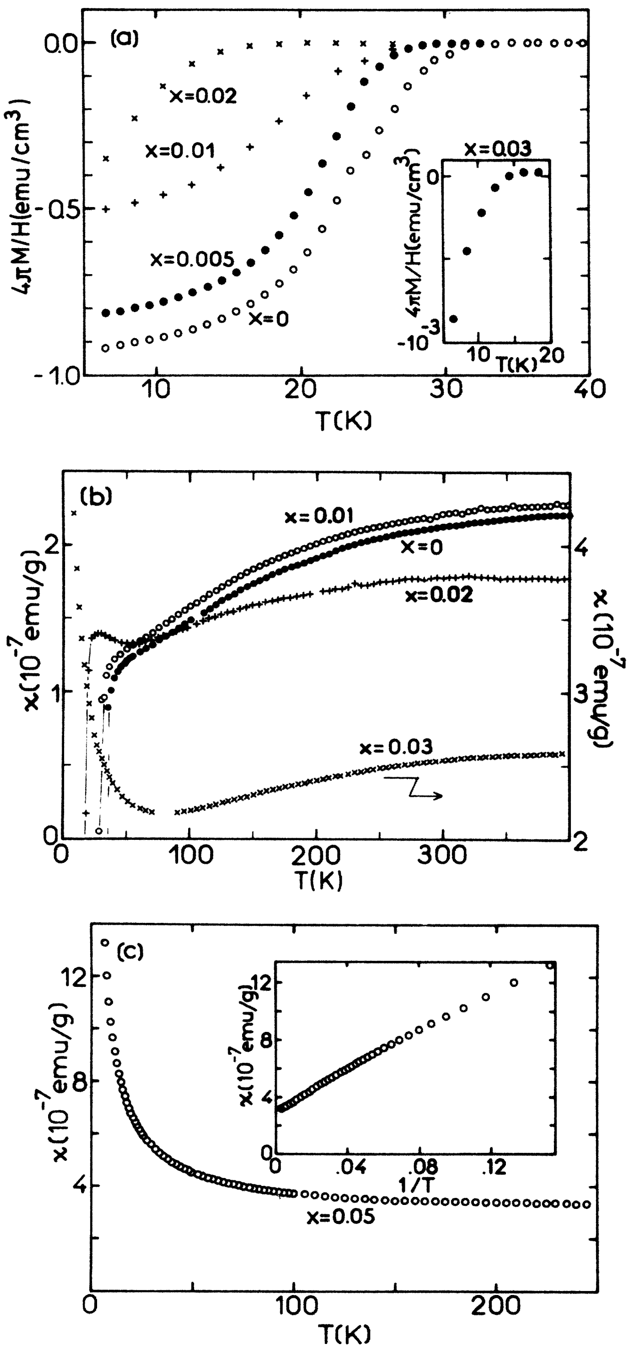

FIG. 4. Magnetization measurements below T_c [(a)] and temperature dependence of magnetic susceptibility above T_c [(b,c)] of $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_{4-y}$.

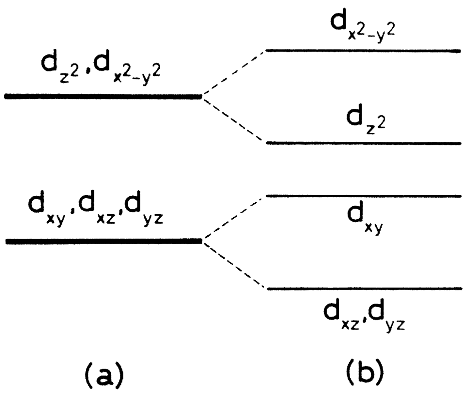

FIG. 5. Splitting of $3d$ orbitals by crystal field in different environments (a) octahedron and (b) elongated octahedron as for La_2CuO_4 or La_2NiO_4.

smaller than the effective moment $\sqrt{3}\mu_B$ of spin $\frac{1}{2}$.

We are first concerned with the understanding of the low magnetic moment carried by Ni atoms. In a perfect octahedral environment, the $3d$ orbitals are split according to Fig. 5(a), with the d_{z^2} and $d_{x^2-y^2}$ orbitals forming two degenerate upper levels. In this case, the "Hund's rule" coupling leads to a spin-1 state of the $Ni^{2+}(3d^8)$ atom, both the d_{z^2} and $d_{x^2-y^2}$ orbitals being singly occupied. In the La_2CuO_4-type compounds, the octahedra are considerably elongated and consequently there is an additional splitting between $d_{x^2-y^2}$ and d_{z^2} [Fig. 5(b)].[13] The $Ni^{2+}(d_{x^2-y^2})$ level has a large hybridization with the band built on Cu($3d$) orbitals and consequently the electron in this state is delocalized in the conduction band. On the other hand, the single electron in the $Ni^{2+}(d_{z^2})$ level hybridizes only very little with adjacent d_{z^2} levels of copper atoms, and consequently should form a localized spin $\frac{1}{2}$, with an effective moment $\sqrt{3}\mu_B$. Alternatively, the d_{z^2} orbital might form a virtual level in the $d_{x^2-y^2}$ band leading again to a localized spin $\frac{1}{2}$. The reduction to the experimental value of $0.7\mu_B$ can then be attributed to interaction effects between Ni atoms, probably of the Ruderman-Kittel-Kasuya-Yosida type via the conduction band. In this context we may notice that there exists at low temperatures some deviation to a perfect Curie law. Another explanation for the reduction of the moment carried by nickel atoms is the possibility for the narrow d_{z^2} level to be split into two weakly overlapping subbands by Coulomb correlations ($U/W \approx 1$). The small overlap between the subbands could thus account for the effective magnetic moment smaller than the one associated to an isolated spin $\frac{1}{2}$. At this stage it is interesting to recall that the local tetragonal distortion of the oxygen octahedron around the $3d$ element is significantly smaller for Ni^{2+} than for Cu^{2+} ions ($c/a = 1.027$ and $c/a = 1.263$, respectively).[14,15] It has thus been suggested that the $d_{z^2} - d_{x^2-y^2}$ splitting should be much smaller for La_2NiO_4 than for La_2CuO_4 with a possible overlap between the localized Ni(d_{z^2}) level and the band built on $d_{x^2-y^2}$ orbitals. Moreover, recent magnetic data on La_2NiO_4 support the coexistence in this compound of localized electrons in a d_{z^2} level and of itinerant electrons in a $d_{x^2-y^2}$ giving rise to a spin-density-wave ordering below 200 K.[16] Hence the model we suggest for the energy diagram of dilute impurities of Ni^{2+} in La_2CuO_4 bears some resemblance with the picture proposed for La_2NiO_4.

Next, what kind of information can be obtained from these experimental results concerning the superconducting critical temperature?

Superconductivity is well known to be extremely sensitive to magnetic impurities and usually a concentration of the order of 1% in regular superconductors is sufficient to destroy superconductivity completely.[17] In the present case about 4% are needed. For a conventional *s*-wave superconductor, this can be explained assuming a relatively small exchange integral between localized spins and itinerent electrons and also in noticing the unusually high transition temperature in the absence of magnetic impurities T_{c0}. According to Ref. 17 the critical concentration for destruction of superconductivity is proportional to T_{c0}/J^2 (note also that J is the Hund's rule coupling between nickel d_{z^2} and $d_{x^2-y^2}$ orbitals and therefore should be of ferromagnetic sign).

However, this simple interpretation of T_c lowering by magnetic impurities is in obvious contradiction with results showing that the effect of zinc impurities is about twice as large as that of nickel.[11,18] Taking the picture discussed above for Ni^{2+}, a Zn^{2+} ion has two electrons in the d_{z^2} orbital and therefore has no localized moment. On the other hand, contrary to Ni, it constitutes a *charged* impurity: The nuclear charge seen by the $d_{x^2-y^2}$ conduction band is not completely screened by the valence electrons. A strong dependence of T_c on nonmagnetic impurities certainly is quite unusual in conventional superconductors. It may, however, have a natural explanation in terms of "anisotropic" superconductivity as proposed for conductors of low dimensionality: quasi-one-dimensional organic superconductors[19] or *d*-type superconductivity recently proposed by a number of authors for La_2CuO_4-type materials.[20–23] In this case, normal impurities are pair breaking in the same way as magnetic impurities, and the effect of magnetic impurities is strongly reduced with respect to the isotropic case.[24] These points certainly are in agreement with the observed much stronger effect of nonmagnetic but charged impurities such as zinc as compared to magnetic but neutral nickel.

However, a number of alternative explanations are also possible, or may act in conjunctions with pair breaking. For example, zinc impurities will change the Fermi level, and if the high T_c is related to the fact that the Fermi level is in the vicinity of a van Hove singularity,[20,22,25,26] this effect alone may affect T_c considerably. Also, localization effects due to increased disorder may play a role. Clearly, both a better understanding of disorder effect in theoretical models for high-T_c superconductors and more systematic experimental investigations are needed.

In summary, we have presented the results of an exhaustive experimental study of the effect of Ni substitution on magnetic, transport, and superconductivity properties of $La_{1.85}Sr_{0.15}CuO_{4-y}$. The salient feature is a reduction of the magnetic moment carried by Ni^{2+} ions which has been attributed to a slightly occupied $Ni(d_{z^2})$ level whereas the $Ni(d_{x^2-y^2})$ level is hybridized with the $Cu(d_{x^2-y^2})$ levels.

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