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BRIEF COMMUNICATIONS

Preparation and Properties of Fluorine-Doped Nd_2CuO_{4-y} Superconductors

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Details of the synthesis, characterization, and superconductivity of fluorine-doped Nd_2CuO_{4-y} are reported. Speculations are made on the likely substitutional site for fluorine and the possibilities of beneficially extending fluorination to other high-T_C compounds. © 1990 Academic Press, Inc.

Until early this year, all high-temperature superconductors containing copper oxide, beginning with the original discovery (*1*), have possessed excess positive charge with respect to a nominally Cu^{2+} ionic state. Now a number of compounds, based on the Nd_2CuO_{4-y} structure (*2–5*), have been synthesized (*6, 7*) which exhibit high-temperature superconductivity yet where the net unit charge, again with respect to nominal Cu^{2+}, is negative. Among these compounds is the first example of an anion-doped high-T_C material, $Nd_2CuO_{4-y-x}F_x$, recently discovered by James, Zahurak, and Murphy (*8*) (hereafter JZM). Although the literature contains many references of attempts to make or enhance high-temperature superconductors by doping with fluorine (*9*), $Nd_2CuO_{4-y-x}F_x$ represents the only successful example to date. In this note, we report confirmation of superconductivity in this compound, along with details of our synthetic approach and characterization.

We followed the usual solid state reaction procedures associated with calcining most high-T_C ceramics. Appropriate molar quantities of dry, spectroscopic grade Nd_2O_3, NdF_3, and CuO were mixed, ground in an agate mortar, and fired in flowing argon for 36 hr at 920°C. The resulting product was, in two repetitive cycles, ground, pelletized, and sintered over a total of 24 hr again at 920°C, after which it was rapidly (30–60 sec) quenched to near room temperature while held in argon.

Although our synthesis approach is similar to that of JZM, it does differ in that we use Ar instead of N_2 as the ambient for both the calcining and sintering steps. We find Ar allows the use of a higher sintering temperature (920 as opposed to 890°C by JZM). In our furnaces, using N_2 at this temperature led to reductive decomposition of the sample. At this time, we do not understand

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completely the underlying reasons behind this behavior, but perhaps it is due to small amounts of contaminants in our laboratory "house" nitrogen. JZM do not describe at what rate they cooled their samples; however, we found rapid quenching necessary to obtain optimum superconducting behavior. Slow cooling always resulted in only trace amounts of superconductivity. Like JZM, we also found our final product to differ significantly in fluorine content with respect to the starting mixture. Using our procedures, a $Nd_2O_3 : NdF_3$ ratio expected to give $x = 0.6$ in $Nd_2CuO_{4-y-x}F_x$ actually resulted in $x = 0.25$ as determined by electron beam microprobe analysis. This final fluorine content, yielding $Nd_2CuO_{3.75-y}F_{0.25}$, resulted in our best superconductor (highest T_C, sharpest transition) and appeared by microprobe uniformly distributed throughout the sample. Powder X-ray diffraction data for this sample is shown in Fig. 1 along with a computer simulation (*10*) for the Nd_2CuO_{4-y} structure fitted to it. The lattice parameters obtained were $a = 3.952$ and $c = 12.157$ Å, values which are slightly larger and smaller, respectively, than a and c for undoped Nd_2CuO_{4-y} in qualitative agreement with JZM. The principal impurity phase found was NdOF as indicated in Fig. 1, along with a tiny amount of Cu_2O resulting from the reduction of unreacted CuO. Both NdOF and Cu_2O were also detected by microprobe to a level of approximately 3 and 1%, respectively. However, these small quantities of NdOF and Cu_2O do bear on the missing fluorine. Even though our reactions were performed under argon to reduce possible problems associated with water vapor present in air and consequent hydrolysis of NdF_3, NdOF can still be obtained due to the reaction of NdF_3 with Nd_2O_3 (*11*).

Figure 2 shows the resistivity data for our $Nd_2CuO_{3.75-y}F_{0.25}$ sample. The normal state is nonmetallic, in the sense that $d\rho/dT < 0$; however, we believe this behavior to be extrinsic and indicates the currently primitive state of $Nd_2CuO_{4-y-x}F_x$ synthesis and processing, inasmuch as $Nd_{2-x}Ce_xCuO_{4-y}$ ceramic material can now be made with positive $d\rho/dT$ throughout the entire normal state between T_C and room temperature (*12*). The overall magnitude of the resistivity is somewhat higher than the best sample shown by JZM, but well within the uncertainties common to four-probe measurements on ceramic samples of varying density. Onset of superconductivity occurs at 20 K with zero resistance at 16 K. We have had some samples which show onsets at 27 K, but which did not reach zero resistance by 5 K. It remains to be seen whether these various vagaries in normal state and superconducting properties are dominated process-induced microstructural inhomogeneities such as the superlattices observed in the $Nd_{2-x}Ce_xCuO_{4-y}$ materials (*13*). Measurements by ac susceptibility indicated 10–15% volumetric superconductivity in our present best samples. This result was also confirmed by dc magnetometry. The thermoelectric power was small, 1–2 μV/K, and negative down to T_C, in agreement with our results on $Nd_{2-x}Ce_xCuO_{4-y}$ (*14*).

The inset to Fig. 1 shows the unit cell of Nd_2CuO_{4-y} with one of the O(1) positions substituted by F in accord with the stoichiometry of $Nd_2CuO_{3.75-y}F_{0.25}$. We propose O(1) as the site most probable for fluorine substitution for much the same reasons as JZM. Since the source of fluorine is NdF_3, it seems reasonable to assume that most F will stay attached to its parent Nd atom throughout calcination. Several attempts were made to introduce fluorine in the CuO plane by using CuF_2 instead of NdF_3 as the dopant source, but no superconductivity could be obtained in the resultant product. These failures indirectly suggest F does not enter the CuO plane when the source is NdF_3. Fluorine substitution on the CuO plane is known to be detrimental to super-

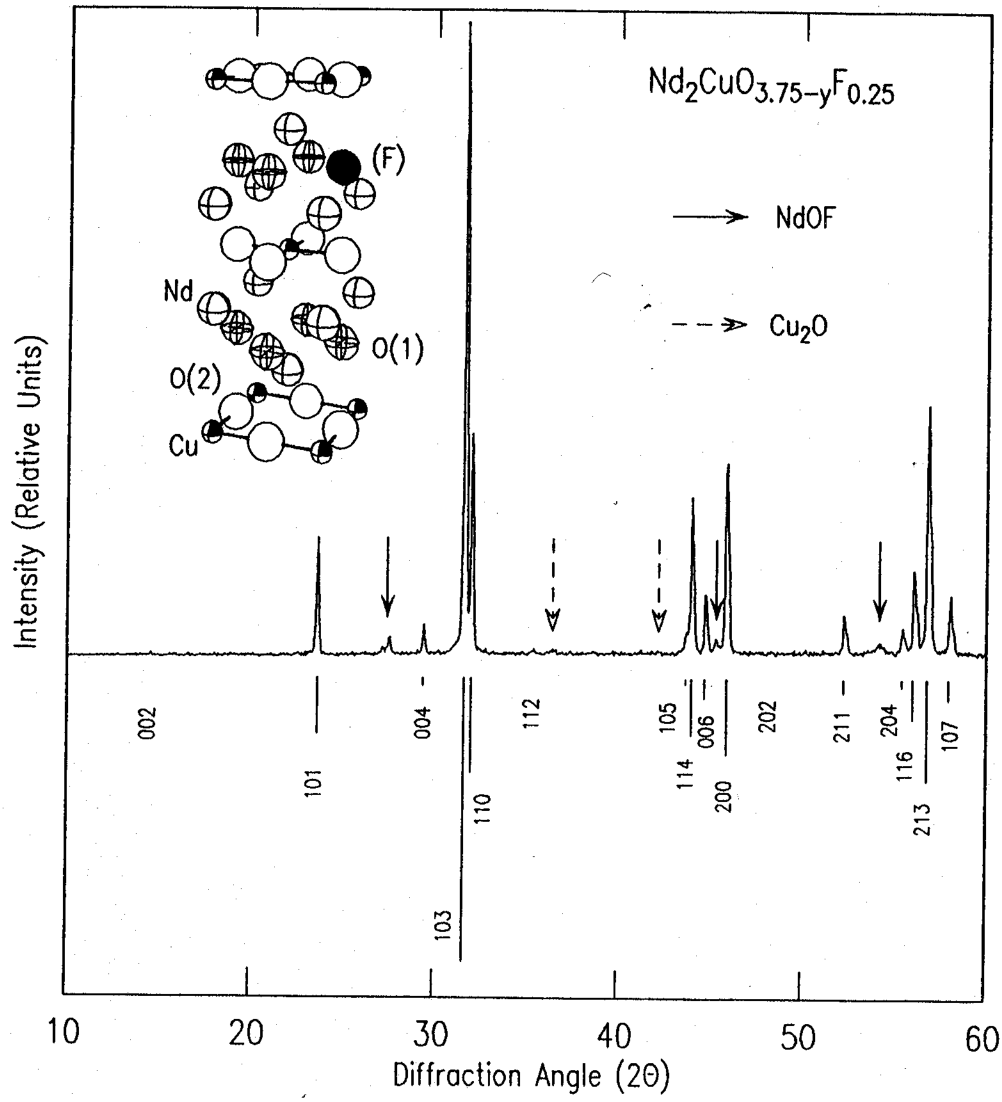

FIG. 1. Powder X-ray diffraction pattern of the $Nd_2CuO_{3.75-y}F_{0.25}$ sample reported here. The stick diagram in the bottom third of the figure is a simulation of the expected pattern using the program Lazy-Pulverix (*10*). The unit cell parameters obtained by fitting the simulated reflections to the measured pattern were $a = 3.952$ and $c = 12.157$ Å. The principal impurity phase observed is NdOF, in addition to a small amount of Cu_2O. The inset contains a perspective view of the Nd_2CuO_{4-y} unit cell. The various element spheres are drawn to half-scale of their ionic radii with respect to the unit cell dimensions. Also indicated on an O(1) site is the presence of one fluorine atom per unit cell, in accord with the sample proportion of fluorine to oxygen. See text for further discussion.

conductivity in the *p*-type compounds (*9*), not only because it removes carriers but also because it would tend to turn the metallic-behaving planes into semiconducting CuO chains (*15*). It thus seems to us that for fluorination to lead to *n*-type superconductivity, the substitution must be at an oxygen site not structurally intimate

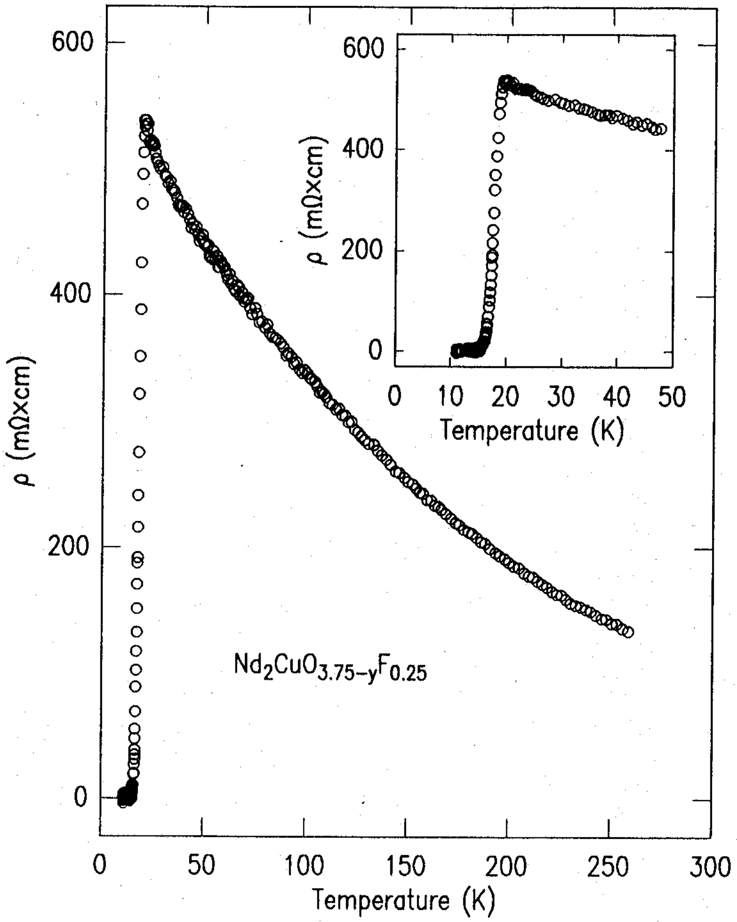

FIG. 2. Resistivity of $Nd_2CuO_{3.75-y}F_{0.25}$ ceramic pellet. Insert shows region near superconducting transition. The upper limit to measured resistivity below T_C, as set by the signal-to-noise ratio of our lock-in detector, was approximately 0.5 mΩ × cm.

with the CuO planes as is indeed true for Nd_2CuO_{4-y}. Thus we would *not* expect fluorination to work for planar CuO compounds which do not have an ancillary, nonapical oxygen site outside the CuO plane available for potential fluorine occupation. An example of such an unsuitable structure is given by the $Ca_{0.86}Sr_{0.14}CuO_2$ compound (*16*). The number of candidate systems suitable for fluorine doping seems quite restricted at present.

Last, it is interesting to note that $Nd_2CuO_{3.75-y}F_{0.25}$ is yet one more example that the optimum carrier concentration for superconductivity is in the range 0.15–0.25 carriers/CuO_2 molecule. This rather narrow interval applies to the whole panoply of planar copper oxide superconductors regardless of unit cell structure or carrier sign. Perhaps if all experimental uncertainties (oxygen content, cation vacancies, etc.) regarding actual carrier concentration in each material were to be somehow settled, there would ultimately emerge only a single universal carrier concentration which can give rise to bulk high-temperature superconductivity.

In summary, we have confirmed the report of superconductivity in fluorine-doped Nd_2CuO_{4-y} by James, Zahurak, and Murphy (*8*). Our synthetic approach, although similar, explicitly finds rapid quenching necessary to obtain superconductivity, a fact which may prove useful in future optimization of these materials. Finally, we speculate that extension of fluorination to other CuO systems may prove difficult if the structural conditions set by Nd_2CuO_{4-y} must be strictly followed.

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