

**Structural, magnetic, electrical and supraconducting properties
of the high temperature superconductor Nd(SrBa)Cu₃O_{6+z}.
Effect of argon annealing.**

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We have studied the structural and superconducting properties of two samples superconductors Nd(SrBa)Cu₃O_{6+z}. One was a conventionally annealed sample at 450°C in oxygen (O) and the other was heated in argon at 850°C followed by oxygen annealing (AO). The T_c of the sample (O) was 68 K and that of (AO) sample was 78 K. This was confirmed by our AC susceptibility, resistivity and Seebeck effect measurements. Further, there was an enhancement in the shielding and the intergranular critical current. The X-ray and neutron data showed a tetragonal structure, and that the (O) sample had a higher impurity level arising from Nd entering the Sr/Ba sites that may result in a decrease in the carrier density (p) which also was confirmed by our thermopower measurements. A combination of several factors such as changes in the Cu (1) apical oxygen distance, chain oxygen ordering, increase in p and in-phase purity for the (AO) sample may qualitatively account for the observed data

I. INTRODUCTION

The structural and superconducting properties of YBa₂Cu₃O_{6+z} have been well documented.¹ There are at least four distinct crystallographic sites (excluding that of oxygen) - Y, Ba, Cu plane and Cu chain - which can be substituted with different elements. The effect of such substitutions on the structural and superconducting properties has been extensively investigated in order to understand the mechanism of the occurrence of superconductivity at high temperatures.¹ Concentrating on the Y site, it has been established that single-phase LnBa₂Cu₃O_{6+z} can be prepared with the superconducting transition temperature T_c , close to 92 K except in the case of Ln = Ce, Pr and Tb. All these compounds show an orthorhombically-distorted oxygen-deficient tripled-perovskite structure and both the orthorhombic distortion and T_c depend sensitively on the oxygen content (6+z). We recall that in the case of YBa₂-_kSr_kCu₃O_{6+z}, it was shown that T_c , decreased from 92 to 83 K when k increased from 0 to 1 and that for $k > 1.2$, the perovskite structure was not stable.² Though the orthorhombic distortion was always observed²⁻⁴ for fully oxygenated samples ($z > 0.8$) for $k = 1$, the orthorhombic to tetragonal transition temperature T_t decreased as k increased⁵ and further T_t depended on the oxygen pressure.⁶ It is interesting to check if an isovalent substitution of Ba by Sr would modify some of the results discussed above when Y is replaced by other rare earths. With these in mind several authors⁷⁻¹⁰ have studied the structural and superconducting properties of Y_{1-x}Ln_xSrBaCu₃O_{6+z}. However, we came across a few contradicting results in the literature. For example, in the case of NdSrBaCu₃O_{6+z} Wang, Hellerbrand, and Bäuerle⁸ reported a tetragonal structure with $a = 3.870$ Å and $c = 11.622$ Å and a $T_c = 74$ K, whereas Badri, Varaadaraju, and Subba Rao⁹ observed $a = 3.865$ Å and $c = 11.640$ Å but with a lower $T_{c \text{ onset}} = 58$ K. Whereas Wang et al.⁸ cooled the samples in flowing oxygen from 900 °C to 600 °C and then to room temperature at a rate of 60°C /h, Badri et al.⁹ annealed the samples in oxygen at 450°C for more than 48 h. Further, no magnetic measurements were reported. In order to resolve this controversy we have investigated the structure

by x-ray-diffraction (XRD) and neutron diffraction, and measured the AC susceptibility, resistivity and thermopower of such samples. In addition we examine the effect of argon heat treatment followed by oxygen annealing that has considerable influence on the structural and superconducting properties.

II. EXPERIMENTAL TECHNIQUES

The polycrystalline samples have been prepared by solid-state sintering of the respective oxides or carbonates. The chemicals were of 99.999% purity except in the case of BaCO₃ which was 99.99% pure. Nd₂O₃, SrCO₃, BaCO₃, and CuO were thoroughly mixed in required proportions and calcined at 950°C in air for a period of 12-18 h. The resulting product was ground, mixed, pelletized and heated in air at 980°C for a period of 16-24 h. This was repeated twice. The pellets (about 10 g) were annealed in oxygen at 450°C for a period of 60-72 h and furnace cooled. This was denoted as sample (O). About 5 g from this batch was heated in argon at a temperature of 850°C for a period of 16 h and the furnace was shut off. When the temperature of the furnace reached about 50°C, the argon flow was shut off and the sample was heated to 450°C in an oxygen flow for about 72 h and the furnace was shut off. This sample was denoted as (AO).

XRD data of the samples were collected with Philips diffractometer fitted with a secondary beam graphite monochromator and using Cu K α (40 kV/20 mA) radiation. The angle 2θ was varied from 20° to 120° in steps of 0.025° and the counting time per step was 10 sec.

Powder neutron diffraction data were collected on 3 g samples of the (O) and (AO) batch in vanadium containers using the medium-resolution time-of-flight diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory, UK. The Rietveld refinement was employed using the program TF15LS at the Rutherford Appleton Laboratory, which is based on the Cambridge Crystallography Subroutine Library.^{11,12} Scattering lengths of 0.769 (Nd), 0.702 (Sr), 0.525 (Ba), 0.7718 (Cu) and 0.5805 (O) (all in units of 10⁻¹² cm) were adopted

[illegible]

Table 2. Refined structural parameters, argon-annealed sample

Atom	Position	x	y	z	B (\AA^2)	Unit-cell occupancy
Nd	Id	0.5	0.5	0.5	0.09(2)	1
Sr/Ba	2h	0.5	0.5	0.1857(2)	0.83(3)	1+1
Cu(1)	1a	0	0	0	0.73(4)	1
Cu(2)	2g	0	0	0.3478(1)	0.22(2)	2
O(1)	4n	0.071(3)	0.5	0	1.3(2)	0.86(4)
O(2)	4i	0.5	0	0.3669(1)	0.35(2)	4
O(4)	2g	0	0	0.1573(3)	1.45(5)	2
P4/mmm: a = 3.8673(1) \AA , c = 11.6550(4) \AA R _p =2.47%, R _{wp} =2.76%, R _{exp} = 1.19%, R _i = 4.44%						

Tables 1 and 2 indicate that the two samples are almost identical with respect to their structural properties and oxygen content and the differences in unit cell dimensions are not considered to be in-significant. Weak unidentified impurity peaks were apparent in both profiles, particularly at d-spacings higher than those used for the refinements but these indicated different impurities in the two samples. A slightly higher impurity level was apparent in the oxygen-treated (O) sample. This may suggest that the primary phase may have a very slightly different composition in the two samples.

The only significant structural difference between the samples appears to be the slightly higher isotropic thermal parameter for the O(4) site in the oxygen annealed sample. This temperature factor is, in fact, high for both samples which is to be expected for materials of this type containing a mixture of Sr and Ba ions coordinating to this oxygen. This observation is consistent with a slight difference in the chemical nature of the Sr/Ba site, which could possibly be a different Sr: Ba ratio in this site for the two samples or even the presence of a small amount of Nd in this position in one of the materials. Since the Nd and Sr scattering lengths are quite similar, a small degree of intermixing of these ions would be possible without it being detectable directly using neutron diffraction.

C. AC susceptibility

1) Real part of the AC susceptibility and shielding effect

In Figs. 3.(a) and 4.(a) we show the real part of the AC susceptibility χ' of the samples (O) and (AO), respectively, as a function of temperature and in the presence of externally applied dc fields. The superconducting transition onset T_c of the sample (O) was found to be 68.6 K which was about 6 K smaller compared to that reported (from resistivity data) by Wang et al.⁸ Let us note that Badri and al.⁹ did not observe a drop in resistivity to near 0 K and hence reported only an onset temperature of around 58 K. The sample (AO) showed a higher $T_{c \text{ onset}}$ at 78.4 K. Since the same sample was used for both heat treatments, one can compare the diamagnetic response. One can note that the screening current of the (AO) sample increased considerably compared to that of the (O) sample.

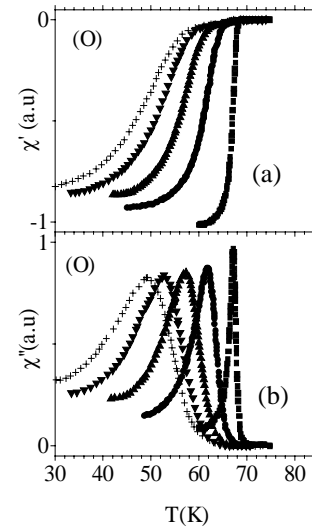


Fig. 3.(a) χ' and (b) χ'' of $\text{NdSrBaCu}_3\text{O}_{6+z}$ (O) as a function of temperature at five different DC fields. Field increasing from right to left 0, 27.5, 56.7, 90.8, 126.5 Oe.

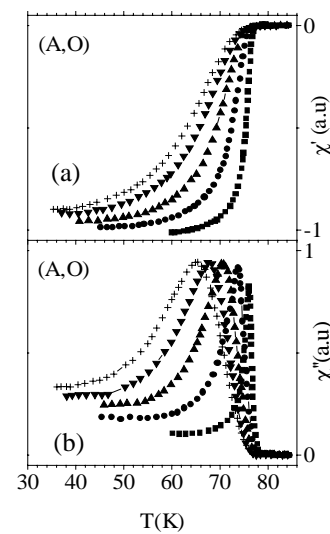


Fig. 4. χ' (a) and (b) χ'' of $\text{NdSrBaCu}_3\text{O}_{6+z}$ (AO) as a function of temperature at five different DC fields. Field increasing from right to left 0, 27.5, 56.7, 90.8, 126.5 Oe.

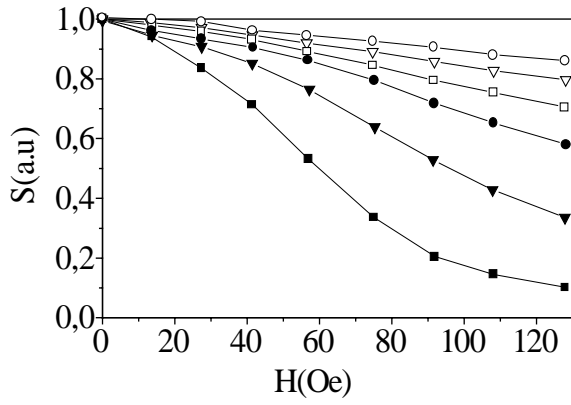


Fig. 5. The shielding effect (S) in arbitrary units as a function of dc field at three different temperatures. Sample (O) \bullet 45 K, \circ 50 K, Δ 55 K; sample (AO) \blacksquare 45 K, \square 50 K, \triangle 55 K.

Let us now look at the real part of the AC susceptibility (Fig. 5) which is nothing but the shielding effect S .¹⁵ The shielding effect S was set arbitrarily equal to 1 for the sample (AO) at 45 K and for $H = 0$. There was a remarkable improvement in the shielding effect in the case of the sample (AO) at all $T < T_c$ and for any applied field. For example at $T = 50$ K, S at a field of 126.5 Oe was a factor of nearly two higher in the case of the sample (AO) compared to that of the sample (O). Further, the decrease in S as a function of the field was much slower in the case of the sample (AO). For example, at $T = 50$ K, the sample (AO) showed a decrease in S of about 20% as the field was increased from 0 to 126.5 Oe whereas the sample (O) showed a decrease of nearly 70%.

2) Imaginary part of the AC susceptibility and irreversibility line

The imaginary part of the AC susceptibility χ'' of the samples (O) and (AO) as a function of temperature at selected applied fields is shown in Figs. 3(b) and 4(b) respectively. The width of the transition was smaller in the case of the sample (AO) at all fields and the peak T_p shifted less with the applied field compared to that in the case of the sample (O). In fact, when H is plotted as a function of $t = T_p / T_c$ in Fig. 6 (a), an enhancement of the irreversibility line was observed due to argon treatment. The data can be analyzed with the help of the following relation¹⁶ $H = K(1 - t)^n$. Straight line plots (Fig. 6(b)) were obtained when $\ln H$ was plotted against $\ln(1 - t)$. The value of K was estimated to be 620 and 1900 Oe respectively for the samples (O) and (AO). Following an earlier result,^{17, 18} K may be interpreted as the field necessary to reduce the intergranular critical current to zero in the limit of $T_p = 0$ K. We note that the argon treatment considerably increases the value of K indicating an improvement in the pinning properties.

D. Resistivity

The resistivity (ρ) of the two samples as a function of temperature is shown in Fig. 7. The data points for the sample (AO) lie clearly below those for the sample (O). In

both cases, ρ reduced to zero at 66 K and 77 K respectively for the sample (O) and (AO). These values are in good agreement with that obtained from the AC susceptibility measurements

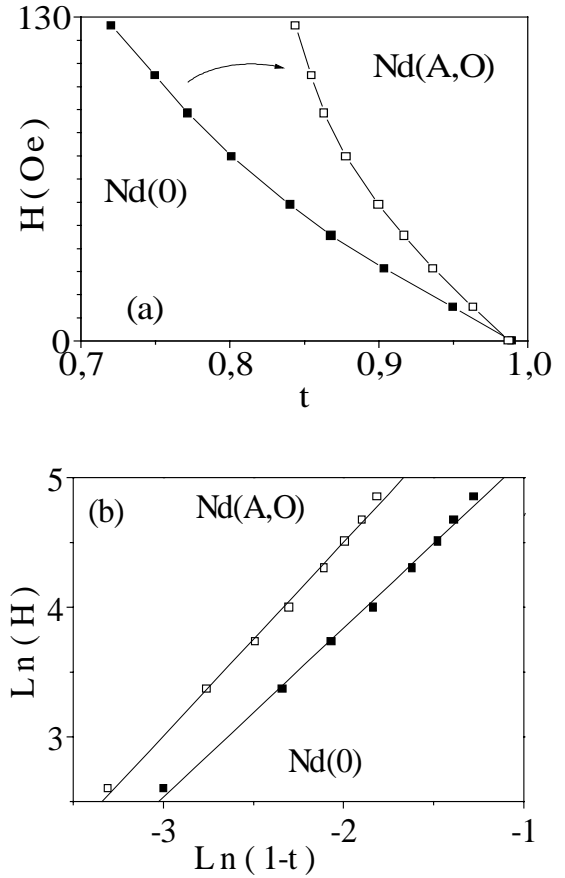


Fig. 6. (a) $t = T_p / T_c$ as a function of H for the two samples (O) and (AO). (b) $\ln H$ as a function of $\ln(1 - t)$ for the two samples (O) and (AO).

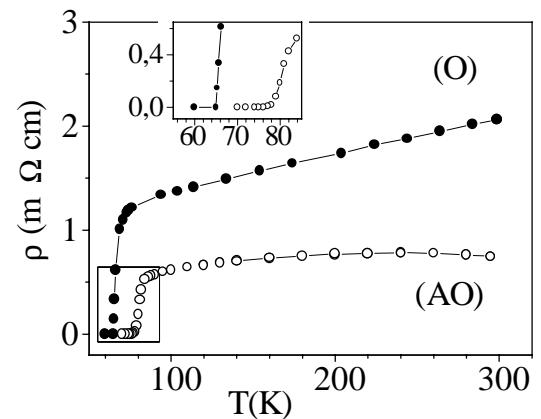


Fig. 7. Resistivity of the samples (O) and (AO) as a function of temperature

Note that for a given thermal treatment $T_{c \text{ onset}}(\chi')$ is superior to $T_c(\rho = 0)$ of 1 to 2 K with $T_p(\chi'') \approx T_c(\rho = 0)$. The measure of the resistance introduces the resistance of contacts

whose is added to that of the sample and reduced $T_c(\rho=0)$. In the normal state, the linear part of $\rho(T)$ obeys the relationship $\rho = \rho_0 + \alpha T$, where ρ_0 is the residual resistance extrapolated to $T = 0$ K and α is the slope $d\rho/dT$. The sample (O) has $\alpha = 3.53$ ($\mu\Omega \text{ cm} / \text{K}$), $\rho_0 = 1016$ ($\mu\Omega \text{ cm}$) and $\rho_{297\text{K}} = 2056$ ($\mu\Omega \text{ cm}$). The treatment (AO) reduced considerably these parameters (Fig. 7.); in particular α (AO) = 1.42 ($\mu\Omega \text{ cm} / \text{K}$). This indicates a diminution of the interaction of carrier charges-phonons. Note that the linear part of $\rho(T)$, of the sample (AO), is between 110K and 230K in good agreement with that of the thermoelectric power (S') (Fig.8).'

E. Thermoelectric power

The thermoelectric power (S') of the two samples as a function of temperature is shown in Fig. 8. The data points for the sample (AO) lie clearly below those for the sample (O). In both cases, S' reduced to zero at temperatures that correspond to T_c of the respective samples obtained from the AC susceptibility and resistivity measurements with $T_p(\chi'') \approx T_c(S' = 0)$. The (O) sample, however, showed a broad maximum before S' reached zero. In the case of the (AO) sample, S' decreased slightly as T decreased from 290 to 230 K and then increased up to around 110 K.

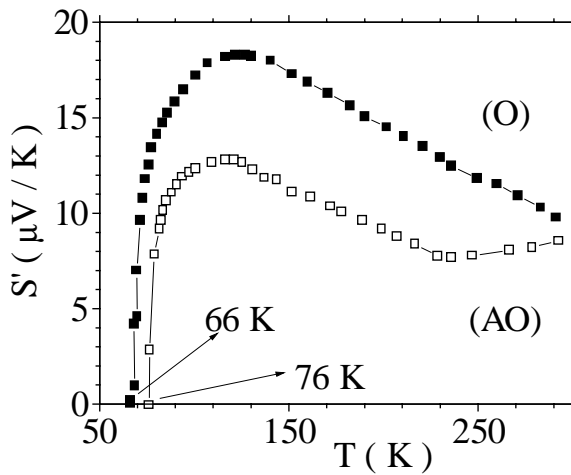


Fig. 8. Thermoelectric power (S') of the samples (O) and (AO) as a function of temperature

IV. Discussion

In the absence of a detailed microstructure analysis of these samples, we propose a qualitative model to understand the present data. The exact reason for the change in the symmetry from orthorhombic to tetragonal when Y is replaced by Nd in $\text{YSrBaCu}_3\text{O}_{6+z}$ is not known. We would like to suggest, however, that a tetragonal structure can be obtained from an orthorhombic structure by rearranging the oxygen vacancies in the ab (basal) plane. On the other hand, there exists the possibility that this treatment (AO) could result in an increase in the ordering of oxygen in the ab plane. It is interesting to note that such a possibility has been suggested¹⁹ in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$. Gupta and Gupta have further proposed that

such a tetragonal structure would even lead to a higher T_c . This structure was also earlier suggested²⁰ for the $\text{LaBaACu}_3\text{O}_{6+z}$ (A=Sr,Ca) family of superconductors on the basis of x-ray-diffraction and electron microscopy data. de Fontaine²¹ also had earlier indicated that a tetragonal structure for $\text{YBa}_2\text{Cu}_3\text{O}_7$ could indeed be stable based on a two dimensional Ising model. Arabi and al²² determined the atomic positions for $\text{HoBa}_2\text{Cu}_3\text{O}_{6+z}$ in tetragonal space group with $T_c=91.5$ K.

We will attempt a qualitative interpretation of our thermopower data in the light of several, earlier reported data and analyses of cuprate superconductors²³. In general, S' of cuprate superconductors starts with a value very close to zero at T_c and increases with T to positive values reaching a maximum at 10 to 20 K above T_c and decreases steadily with increasing temperature. A minimum value is reached at a certain T and then S' increases again with T . However some exceptions and even contradicting results have been reported. V. Vijayashree and al²⁴ have found a change of sign from negative to positive values as T reached around 40 K. In the case of $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$ samples, S' at 300 K was found²⁵ to have values ranging from -4 mV/K to +8 mV/K as z decreased from 1 to about 0.8.

Several models have been proposed in the past which involve mostly fitting of experimental data²³. It has been shown that the total thermoelectric power S' comes especially from the dominant contribution of the thermal diffusion. Very often S' decreases linearly with T between say 100 K and 300 K. In certain cases, the slope changes between 220 K and 300 K. In the case of the (O) sample, S' can be expressed as $25 - 0.053T$ between 130 and 250 K and in the case of the (AO) sample the expression turns out to be $17.5 - 0.042T$. Kaiser²⁶ calculated the temperature dependence of S' arising from the electron-phonon interaction. Hence the exact cause for the behavior of S' with temperature is yet to be unambiguously explained. It is interesting, at this point, to look at the data of Obertelli and al.²⁷. Keeping in mind that an understanding of the normal-state properties of cuprate superconductors could help in understanding the mechanism of high-temperature superconductivity, these authors have attempted a systematics of S' in several cuprate superconductors as a function of the hole density. Using their data we may conclude that our sample (O) is underdoped and the treatment (AO) favors an increase in the hole density and thus explains the observed increase in the T_c . On the other hand the increase in S' observed between 230 and 300 K in the case of the (AO) sample could arise due to a contribution from another band not involving holes or due to a rearrangement of oxygen atoms in the basal plane or due to a combination of these and several other factors.

Whereas the thermopower data of our samples (O) and (AO) may indicate that there is an increase in the hole density in the sample (AO) relative to the sample (O) that might account for the increase in the T_c , the exact reason for this increase in the hole density cannot be specified. Two possible explanations can be proposed.

A high-temperature treatment in oxygen results in a small degree of Nd entering Sr/Ba positions and this occurs to a reduced extent (possibly not at all) by annealing in Ar. Subsequent low-temperature oxygen anneal of the Ar preheated sample results in oxygen uptake but the temperature is too low for any cation rearrangement. Our XRD and neutron data showed that the usual oxygen-annealing, (O) sample, had a higher impurity level than the (AO) sample. Nd entering the

Sr/Ba sites might be expected to result in a further increase in the 0 (4) temperature factor which is bonded; to this site. This was what we observed. Further Nd on the Sr/Ba sites with no appreciable change in oxygen content would result in a decrease in the carrier density for the (O) sample which is consistent with the thermopower data. We note that similar effects were reported²⁸⁻³⁰ in the case of $\text{LaBa}_2\text{Cu}_3\text{O}_7$. This compound can only be made pure (without La on the Ba sites) by initially heating in 0 free atmosphere and then using the low-temperature oxygen anneal. Further, it is likely that the spatial variation of the superconducting order parameter would then decrease resulting in an improvement in the shielding properties as observed here.

As for a second plausible explanation, it may be relevant to discuss the results³¹ obtained on the nuclear quadrupole resonance (NQR) spectra of $\text{LnBa}_2\text{Cu}_3\text{O}_{6+z}$, (Ln=Y, Nd). Briefly, these authors established a relation between the number of oxygen atoms per chain (noc), the oxygen index ($6 + z$) and T_c . It was found that the noc is a function of z and that noc determines T_c . A minimum noc is required to observe superconductivity in these cuprates. For a given z , the noc and hence the T_c , can be different in the $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$, and $\text{NdBa}_2\text{Cu}_3\text{O}_{6+z}$ compound. The increase in T_c in $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$ as a function of z is normally attributed to an increase in the orthorhombicity and to an increase in the oxygen ordering in the a - b plane. Now, our neutron data (Tables 1 and 2) and the iodometry measurements indicated that the total oxygen content in both the cases was close to 6.85 and thus there was hardly any change as a result of the argon treatment. Thus the reason for the increase in T_c may lie in some other factor than z . We propose, hence, that a rearrangement of oxygen atoms in the basal plane following the (AO) treatment would have caused an increase in the noc and this in turn would increase T_c . A detailed NQR study of our samples would be highly desirable in this respect.

Concerning the irreversibility line, we would like to make short comments. Both the imaginary part of the AC susceptibility and the DC magnetization are used to establish such a line, some favouring the latter technique¹⁵. Some authors have used both the techniques on the same sample and have shown that in the case of a single crystal³² of YBaCuO or $\text{Bi}(2212)$, the irreversibility line obtained from the AC technique (at frequencies of the order of 1000 Hz) coincided with that obtained from the DC technique whereas in the case of polycrystals, the irreversibility line obtained from the AC technique was found to lie lower in the H - T plane^{32,33}. However, any enhancement in the

irreversibility line of a given sample due to substitution or heat treatment was reflected in both types of measurements³³. It is only this aspect - enhancement in the irreversibility line due to heat treatment - that we wanted to emphasize. Vanacken et al³⁴ have measured, the field-cooled and zero-field-cooled DC magnetization of $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$ as a function of z to establish the irreversibility line and analyzed their data using the relation $H = K(1 - t)^n$. They showed that n was independent of z but T_c and K (and also the orthorhombicity) increased steadily with z indicating possibly the role played by an increase in oxygen ordering. Slight differences in oxygenation might also induce changes in Cu 1-6 oxygen apical distance and T_c as was discussed elsewhere^{10,35}. The observed increase in the shielding properties and pinning may also be explained qualitatively by the factors discussed above.

We wish to make a brief comment on the relation between ionic size of the rare earth and T_c as was suggested by Wang et al⁸. These authors have observed a decrease in T_c , from 79 to 74 K when Y was replaced by Nd in $\text{YSrBaCu}_3\text{O}_{6+z}$. Not only our value of T_c of $\text{YSrBaCu}_3\text{O}_{6+z}$ is different (83 K see Ref.18) from that reported by Wang et al. but also the variation in T_c , as Y was replaced by Nd, is different. In fact we found that T_c decreased from 83 to 78 K. Hence we are tempted to believe that the changes observed in T_c , need not be related only to the ionic size of the rare earth but rather to a combination of several factors such as changes in the Cu 1 - apical oxygen distances, oxygen disorder, hole density etc.

A detailed NQR study of our samples and extended to other superconductors with different rare earths may be useful in finding out the role played by certain defects on the superconducting properties.

V. Conclusions

We have investigated the structural and superconducting properties of two samples superconductors $\text{Nd}(\text{SrBa})\text{Cu}_3\text{O}_{6+z}$, the one oxygenated in a conventional manner (O) and the other oxygenated following a heat treatment in argon (AO). Both the samples had a tetragonal symmetry and there was hardly any change in the value of z . Though the sample (AO) showed an increase of 10 K in T_c this has been confirmed by measures of resistance and thermopower. This increase may result from a possible increase in the hole density for the (AO) sample as shown by the thermopower data. The neutron data for the (O) sample indicated the presence of Nd on the Sr/Ba sites that may result in a decrease in carrier density and hence with a reduction in T_c . Also, we have shown that the shielding effect and irreversibility line improved remarkably in the sample (AO).

¹For a detailed discussion and additional references see, B. Raveau, C. Michel, M. Hervieu and D. Grout, in: Crystal Chemistry of High- T_c Superconducting Copper Oxides (Springer, Berlin, 1991).

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