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SUPERCONDUCTORS AND NONSUPERCONDUCTORS IN $Nd_{2-x}Ce_xCuO_4$

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Results are presented on the chemical composition and structure of the n-type superconductors $Nd_{2-x}Ce_xCuO_4$. Electron diffraction and high resolution electron microscopy indicate that there are three slightly different structures, two of which are modulated versions of the first. By matching both the images and diffraction patterns it is shown that the modulations are due to small displacements of the cations, possibly a charge density wave, not simply ordering of the Ce or oxygen vacancies, although oxygen stoichiometry may be the driving force for the modulations. Both types of phases occur in materials which are superconducting, and those which are not. Microanalysis indicates that the Ce content of the superconducting specimens after reduction is slightly smaller at 0.16 rather than 0.19, and the cation stoichiometry is not detectably different between the modulation and unmodulated materials.

1. Introduction

The recent discovery of an n-type superconductor of general formula $Nd_{2-x}Ce_xCuO_4$ has opened up the possibility that there exists a new family of high temperature superconductors. Initially identified as having a Nd_2CuO_4-type structure [1,2], more recent reports have mentioned a second phase which contains a superstructure [3,4]. Although the diffraction data presented in both these later papers is very similar, the exact form of the modulation is presented as different, being either a quadrupling of both (110) and $(1\bar{1}0)$ [3] or a quadrupling of (110) with a doubling of $(1\bar{1}0)$. Important questions are: which phase is the active superconductor; what is the structural and chemical relationship between the modulated and unmodulated phases and what is the correct interpretation of the modulated unit cell? In addition, it has been suggested that the modulations are due to ordering of oxygen defects, a point which needs to be rigorously tested.

In this paper we will show that both interpretations of the modulated structure are in fact correct; there are at least two different possible modulations. We will also demonstrate that the modulations cannot be explained on the basis of oxygen defects alone, but must involve a positional modulation of the cations which we suggest could be a charge density wave.

2. Experimental method

Two $Nd_{2-x}Ce_xCuO_4$ compounds were prepared by the identical solid-state reaction, followed by sintering at 1170°C for 12 h. Of these two samples, one was annealed in pure Ar at 900°C for 3 days, and the other was not.

The results of Meissner effect measurements were carried out in an applied field of 10 Oe under field-cooled conditions. The annealed sample had a substantial signal which indicated an onset of superconductivity at around 21 K with 40% superconducting volume, whereas the unannealed sample showed no superconductivity.

Both superconducting and nonsuperconducting samples were examined in a Hitachi-700 TEM at 200 kV using selected area electron diffraction to identify the reciprocal lattice, in a Philips-400 and a Philips-420 at 120 kV for X-ray spectroscopy to determine the chemistry, and in a Hitachi-9000 at 300 kV for high resolution electron microscopy. For completeness, we show the X-ray data from both the Philips 400 and 420 microscopes, but we suspect the data from the 400 since the Cu/Nd signal was in all

samples significantly low. To assist in interpreting the diffraction patterns and high resolution images, both were simulated on Apollo workstations using the NUMIS software developed at Northwestern University. These image simulations were performed typically with sampling to six reciprocal ångstroms and a variety of different total thicknesses.

3. Results

Consistent in spirit with earlier reports, e.g. [3,4], we found in the samples two variants of the same basic structure; one an unmodulated structure with a tetragonal unit cell and a second which was a superstructure modulation of the first with a larger true unit cell. This is most clearly evident in the diffraction patterns, and fig. 1 shows a montage of diffraction patterns for, on the left, the non-modulated structure and on the right the modulated one. It is apparent that the strong spots in both are the same, which means that the basic structural unit is the same. The modulated structure can, crystallographically, be identified as a quadrupling of the unit cell along [110] and/or [1$\bar{1}$0] coupled with a doubling of the *c*-axis; note for instance in fig. 1 for the [100] zone the existence of spots at $\{0, n+\frac{1}{2}, m+\frac{1}{2}\}$. For a more complete description of the superstructure, we can use a matrix to relate the basic unit cell $\boldsymbol{a}$ to the modulated unit cell $\boldsymbol{a}'$ as

$$\boldsymbol{a}' + \mathbf{M}\boldsymbol{a},$$

where for the one-dimensional modulation normal to *c*:

$$\mathbf{M}_1 = \begin{pmatrix} 1 & 1 & 0 \\ 2 & \bar{2} & 0 \\ 0 & 0 & 2 \end{pmatrix},$$

and for the two-dimensional modulation normal to *c*:

$$\mathbf{M}_2 = \begin{pmatrix} 2 & 2 & 0 \\ 2 & \bar{2} & 0 \\ 0 & 0 & 2 \end{pmatrix} \quad \text{or} \quad \begin{pmatrix} 4 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

The diffraction data can be indexed in principle by either overlapping domains of twin related $\mathbf{M}_1$ as suggested by Williams et al. [4], or by $\mathbf{M}_2$. Using the diffraction data, we can find for the [100] zone evidence for two domains of $\mathbf{M}_1$, since the intensity of the $(0\frac{1}{2}\frac{1}{2})$ is different from that of $(0\frac{1}{2}\frac{\bar{1}}{2})$ and for the [001] zone evidence for $\mathbf{M}_2$ from the existence of spots in locations such as $(1\frac{1}{2}0)$. However, spots in the positions $(1\frac{1}{2}0)$ could be due to double diffraction, and in patterns there is a clear absence of spots at $\{2n+1, 0, 0\}$ which one would not expect for the $\mathbf{M}_2$ structure. As more definitive proof of the existence of both types of modulation, fig. 2(a) shows a lower resolution image in which two dimensional modulations normal to the *c*-axis are clearly evident and fig. 2(b) a diffraction pattern from a grain in which only the $\mathbf{M}_1$ modulation appears. We therefore feel that the experimental evidence favors the existence of both modulated structures, and we suspect that more complicated modulations may also be present.

The identification of a superstructure by electron diffraction does not uniquelly determine in all cases what the structural character of the modulation is particularly since electron diffraction patterns are not kinematical so interpretation of the intensity distribution directly is not feasible. A better characterized experiment in this sense is high resolution electron microscopy, and fig. 3 shows results for the two different structures. It is important to note that the contrast of the structural modulation is quite strong, a point that will be returned to later.

Given that there is a superstructure of some sort, the next question is what is the atomic structure? We have considered four possibilities, namely an ordering of oxygen vacancies (or interstitials, the imaging results will be very similar), see fig. 4(a); an ordering of the Nd/Ce positions, see fig. 4(b); a variation in the Ce–O bond lengths together with a Nd/Ce ordering, see fig. 4c; or a positional modulation, see fig. 4(d). (One can of course combine these.) To identify which is the major source of the image contrast, we performed image and diffraction simulations for the four cases, in all cases only considering the $\mathbf{M}_1$ structure. The results of the simulations are shown in figs. 5 and 6 which show, respectively, simulated diffraction patterns and images to go with figs. 1 and 3 as well as experimental results at the same scale for comparison. It is apparent from these that only the positional modulation comes close to matching the experimental data, and we can rule out

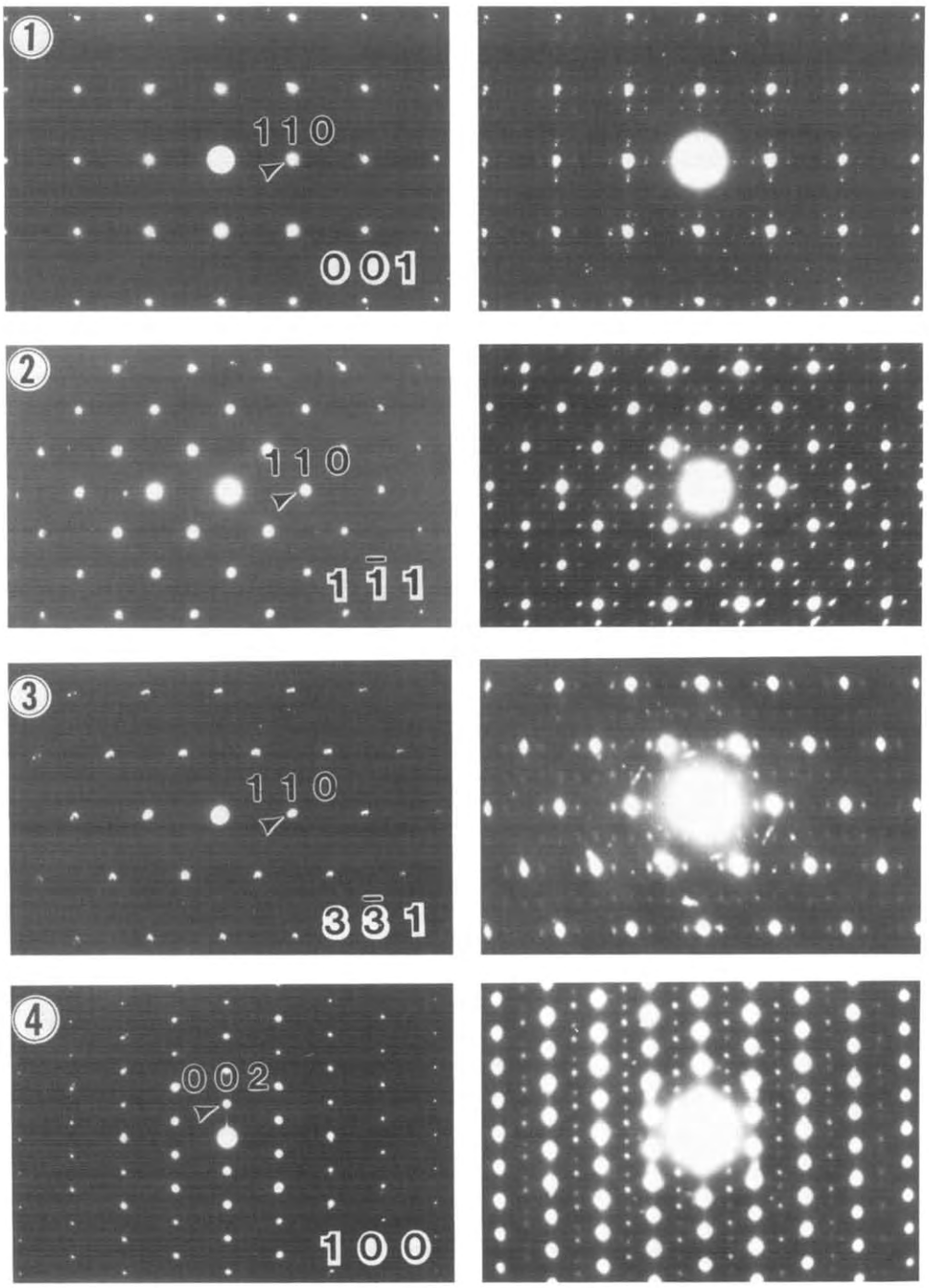

Fig. 1. Diffraction patterns of the unmodulated $Nd_{1-x}Ce_xCuO_4$, left, and modulated structure, right, where down the page (1–4) the zones are [001], [1$\bar{1}$1], [3$\bar{3}$1] and [100], respectively.

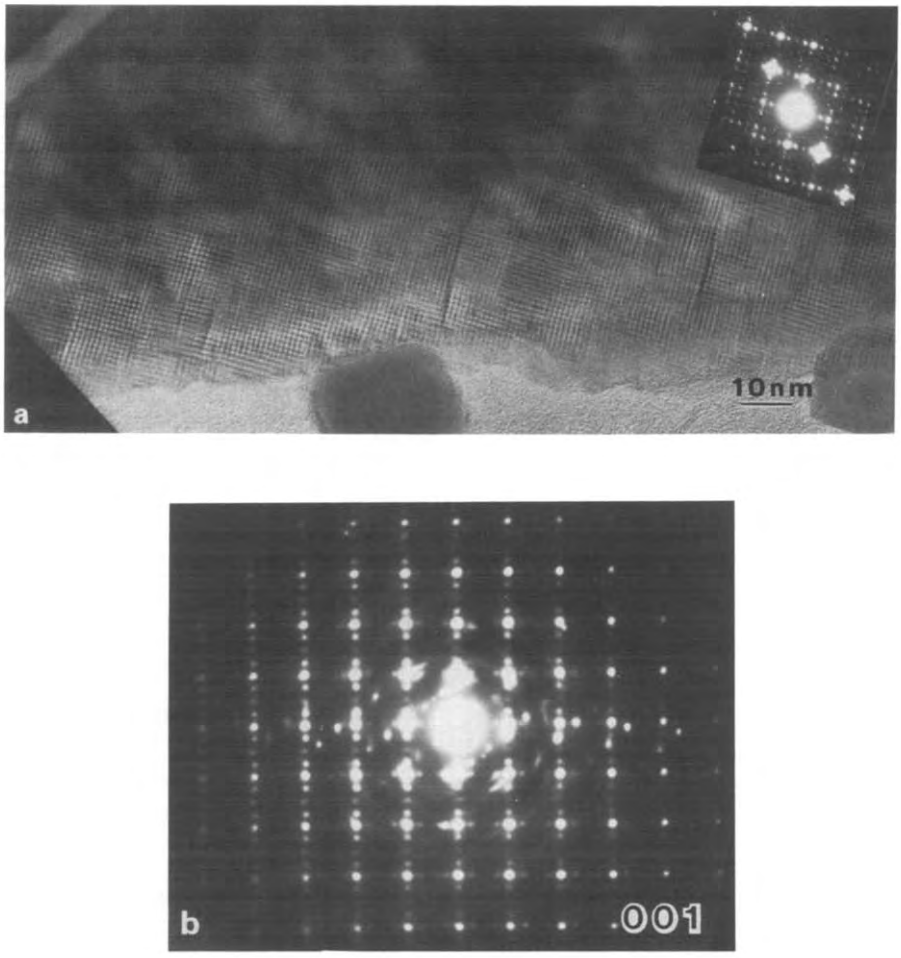

Fig. 2. (a) Low resolution image showing evidence for the M_2 structure as a two-dimensional modulation of the material. The image is along [001]. (b) Diffraction pattern from a grain along [001] in which only one strong set of satellite spots is apparent.

the other possibilities as the *primary* source of the image contrast. We should note that within reasonable experimental error, the M_2 structure can be considered as the superposition of two twin related M_1 structures. This conclusion as to the structure of the material is not surprising since the electron scattering factors for Nd and Ce are very similar, and oxygen is a much weaker scatterer than the cation in the structure; the first three models as expected predict far less contrast than was observed experimentally. Note that we can only identify what is the source of the image contrast, and we cannot state that there are not also changes in the oxygen content or the Ce composition.

To refine at least the question of the Ce content, we analyzed a number of grains both of the superconducting specimen and the nonsuperconductor for the cation composition and the results are summarized in table I. It is clear from the results that there is no major difference between the Ce (and other cation) content between the modulated and unmodulated structures, although interestingly the superconducting unmodulated material was slightly poorer in Ce, this result being significant despite some small scatter in the experimental data. Also shown in table II are the relative populations of the modulated and unmodulated structures in both samples, which show that the modulated structure was more common by

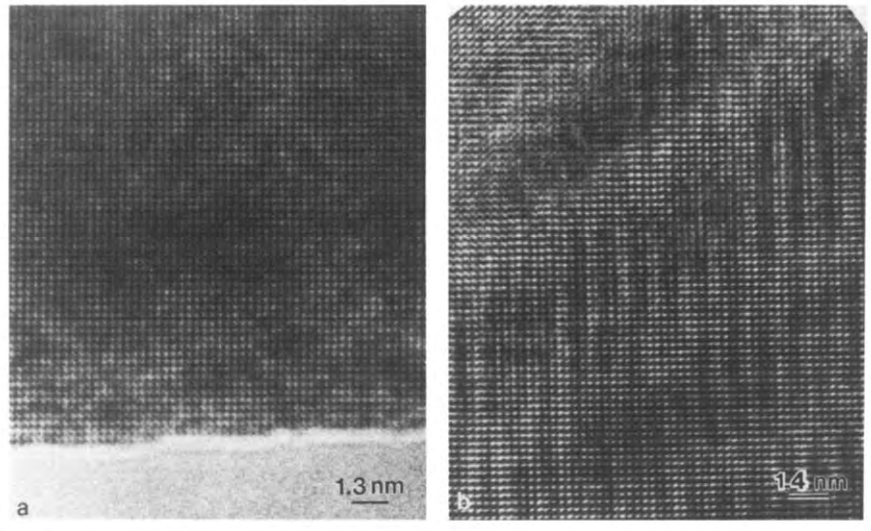

Fig. 3. High resolution images of the unmodulated (a) and modulated (b) structures along [001].

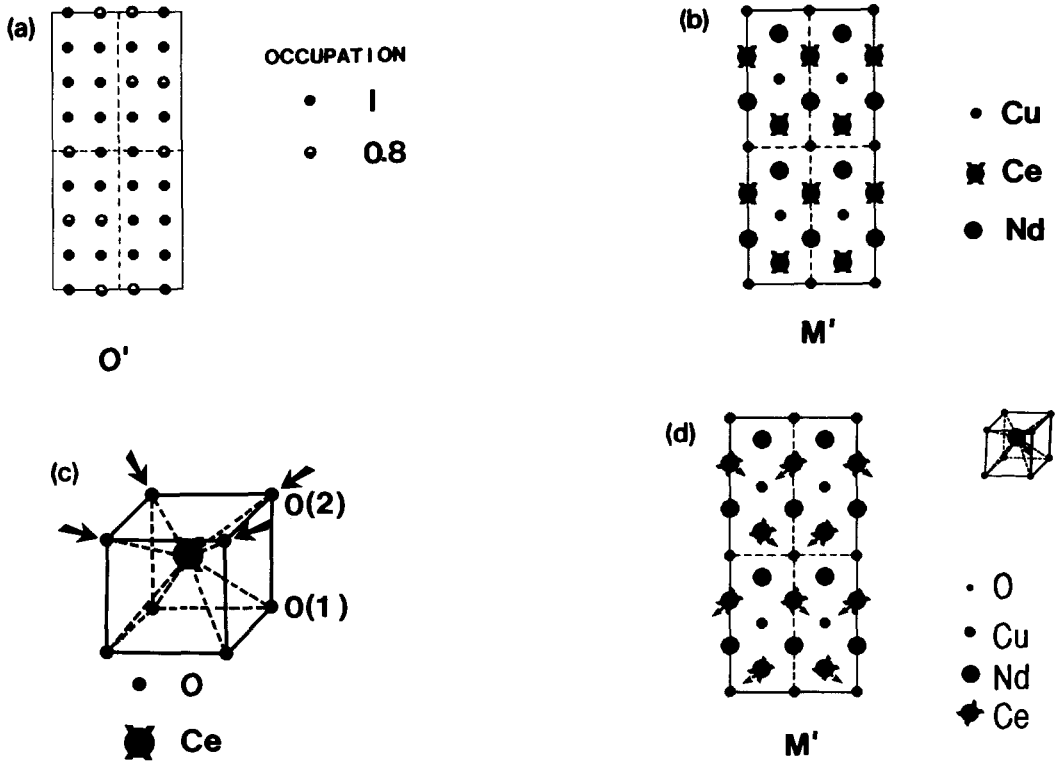

Fig. 4. The four models employed to test the character of the modulated phase: (a) ordering of oxygen vacancies included as an 80% occupancy at the partially shaded sites; (b) ordering of the Ce and Nd; (c) contractions of the local Ce–O bond lengths and (d) a modulation of the cation positions.

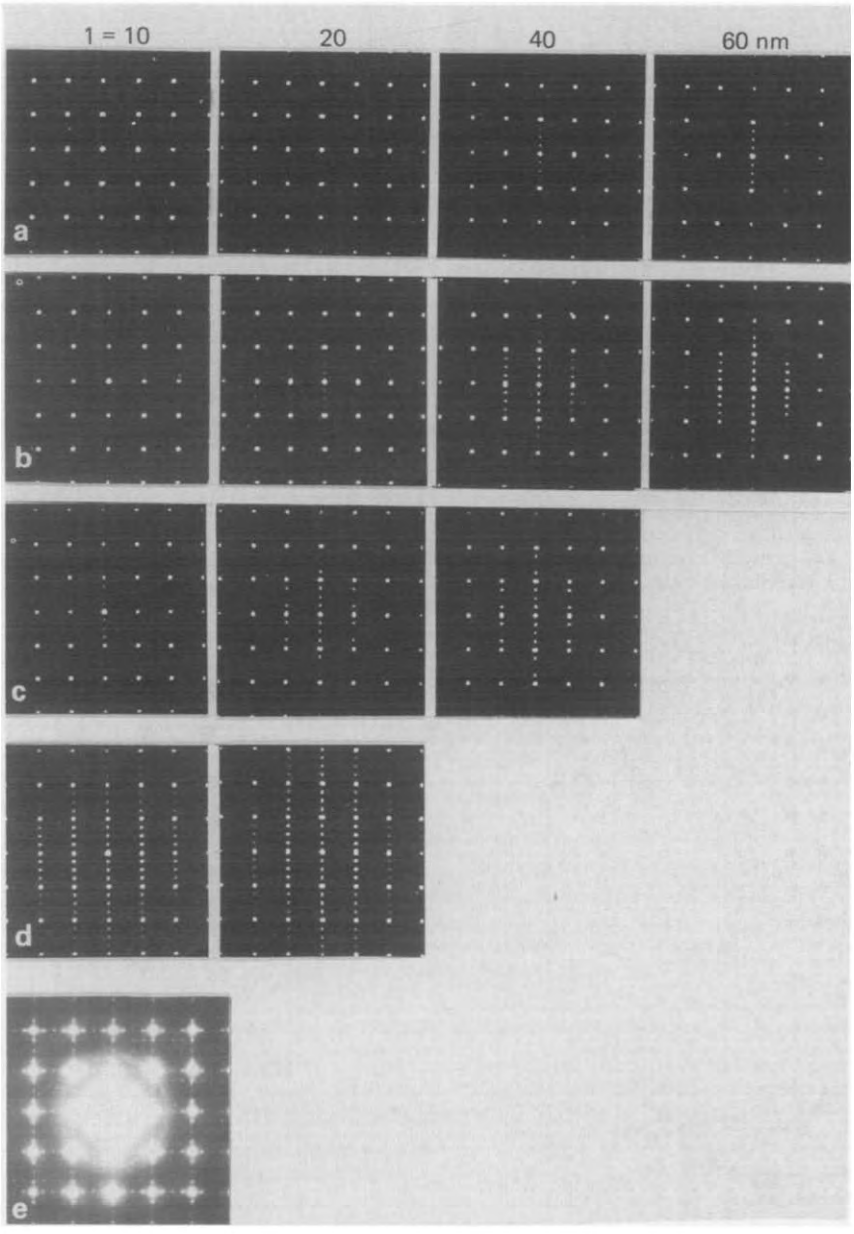

Fig. 5. Calculated diffraction patterns along [001] for different thicknesses where (a)–(d) correspond to (a)–(d) in fig. 4 and (e) is the experimental diffraction pattern along [001] direction. Note that only model (d) gives sufficiently strong satellite spots for the typical experimental thicknesses (10–20 nm).

about a factor of 2 in the unannealed material. The statistical data is consistent with interpreting the modulated structure in both samples as non-superconducting, the unmodulated structure in the annealed sample as superconducting and the unmodulated structure with a reproducible higher Ce content in the unannealed sample as nonsuperconducting.

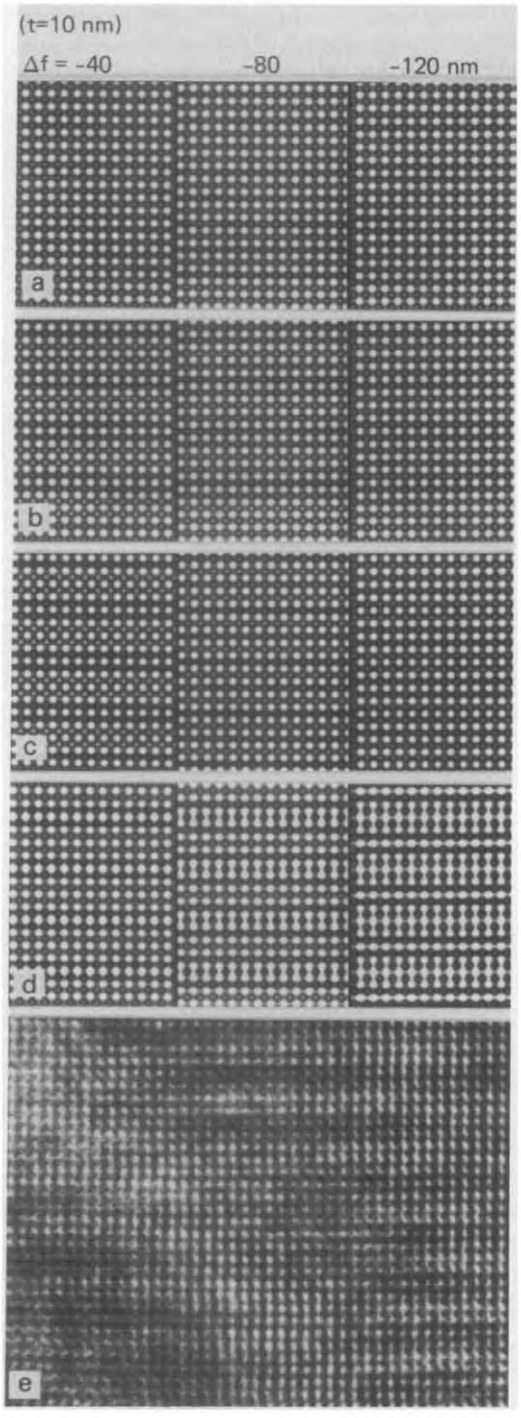

Fig. 6. Calculated image for three different defoci for the four different models as in figs. 4 and 5, all for a thickness of 10 nm. Of the four models, only (d) comes close to giving a reasonable contrast level for the modulations.

Two final results which we will report concern the form of the diffraction patterns away from the major zone axes of the material and radiation damage effects. As an example, fig. 7 shows a diffraction pattern taken from the $[7\bar{7}1]$ zone of the modulated material. It is apparent that the intensity maxima along (110) are oscillating along the orthogonal $(1, \bar{1}, \overline{14})$ direction; this effect is also apparent to a smaller degree in patterns along the $[3\bar{3}1]$ zone axis. A simple interpretation of this would be in terms of a shear wave modulation along [110] similar to the displacement model suggested above.

The second result concerns radiation damage to these materials. During tilting single grains in order to map out the reciprocal space (1–2 h), we noted that originally unmodulated materials transformed into modulated materials, *and* vice-versa in some cases. One interpretation of this is that the modulations vanish for only a particular value or narrow range of oxygen stoichiometries, and the electron beam is displacing oxygen from the material. This conclusion is consistent with reports of modulations in over-reduced samples [4] and in our unreduced samples.

4. Discussion

The results indicate some very interesting features of the $Nd_{2-x}Ce_xCuO_4$ system. The circumstantial evidence indicates that the modulated material is not a superconductor, neither is the material with the higher (0.19) Ce content and that the superconductor is probably the lower (0.16) Ce content, unmodulated material with perhaps a narrow range of oxygen stoichiometry. Since we have not detected any substantial changes in the cation concentrations between modulated and unmodulated materials, we have to suspect that a different oxygen content is driving the modulated structure. The system appears to have some similarities to the older $La_{2-x}Sr_xCuO_4$ system where the optimum superconductor has only a very narrow range of x values, complicated by what we suspect is a charge density wave modulation driven by oxygen defects which can destroy the superconductivity.

It is appropriate for us to compare our results with those of a recent paper by Williams et al. [4] which

Table I
Chemical composition as measured by EDX for the modulated and unmodulated material in both annealed and unannealed sample For some reason the Cu content was consistently low for the Philips 400 microscope. In all cases the existence of modulations was checke from the diffraction patterns near a zone axis.

	Philips 400		Philips 420	
	Ce	Cu	Ce	Cu
Simple Structure				
Annealed Sample	0.16	0.71	0.16	0.92
Number of Crystals	9		8	
STD of results	0.006	0.04	0.02	0.066
Simple Structure				
Unannealed Sample	0.21	0.75	0.19	0.99
Number of Crystals	8		9	
STD of results	0.015	0.062	0.003	0.046
Modulated Structure				
In Both Samples	0.19	0.77	0.16	0.94
Number of Crystals	4		4	
STD of results	0.023	0.028	0.012	0.053

Table II
Populations of the modulated and unmodulated structures based upon diffraction data. No attempt has been made to differentia between the M_1 and M_2 structures.

	Modulated	Unmodulated	Ratio
In superconducting sample	21	36	1:1.7
In nonsuperconducting sample	26	25	1:1

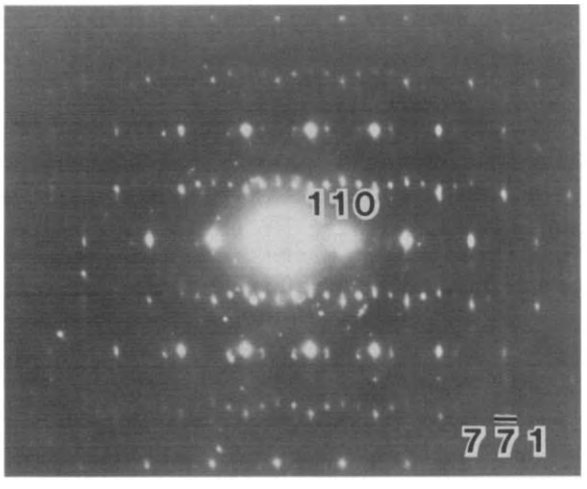

Fig. 7. Diffraction pattern along the [7$\bar{7}$1] zone showing evidence for a shear modulation.

reports very similar results in many respects with smaller number of crystals for the EDX and diffra tion statistics. Both our results and those of Willian et al. imply that the Ce content of 0.16 or 0.15 is su perconducting and has an unmodulated structur and that there is a second material with a higher C content of 0.19 or 0.185 which is also unmodulate but does not superconduct. The latter conclusion also supported by the results of Tokura et al. [5] an Liang et al. [6]. Williams et al. go one step furth in interpretating the images, suggesting that some fir structural details in the thicker regions is due t varying oxygen content within the unit cell. A though this is one interpretation of their results, it important to point out that there is no reason th this should be the correct interpretation. It is we known in high resolution electron microscopy th small errors in the imaging conditions which are a

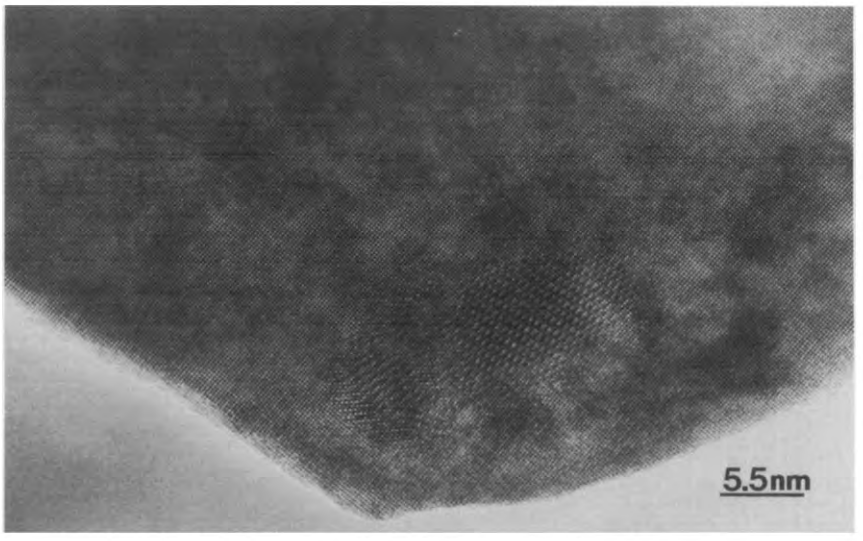

Fig. 8. Image of a small region within an otherwise unmodulated material which can be interpreted as a rotational variant of M_1.

most impossible to avoid in large unit cell materials reduce the symmetry of the apparent unit cell, for instance very small errors in the beam alignment, astigmatism or crystal orientation; for further discussion of these effects see refs. [7–9]. Unit cell symmetries from high resolution micrographs are in general considered suspect, and the only accepted method of determining small deviations from symmetry is convergent beam diffraction from thicker crystals. It is certainly true that high resolution electron micrographs can be sensitive to oxygen contents, although as evidenced by the discussion in the literature, e.g. ref. [10], this is nontrivial but experimentally for the 123 superconductors one can differentiate between [100] and [010] [11].

We should also discuss our interpretation of the modulated structure in this material. Williams et al. [4] report similar results, although they only identified the M_1 modulation and reported no doubling of the *c*-axis. Izumi et al. [3] report the M_2 modulation with no doubling of the *c*-axis, although from their published experimental diffraction patterns fig. 2(b) appears to be the M_1 modulation with twinning similar to our figure. Our results indicate that both interpretations are partially correct. We would also like to add that we have some indications of more complicated modulations, so the phase diagram of structural modulations in these materials may be very complicated, see for instance fig. 8. Obviously additional work on better characterized single crystals is required, and in the light of the modulations in these materials X-ray diffraction results from powder samples treated with some caution.

Acknowledgements

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