

NEUTRON DIFFRACTION STUDIES OF HIGH- T_c SUPERCONDUCTORS*

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CONF-880408--43

DE89 004208

March 1988

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INVITED TALK at the 1988 Spring Meeting of the
 Materials Research Society, Reno, NV, April 5-8, 1988.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences,
 under contract W-31-109-ENG-38.

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Extended Abstract for the 1988 Spring Meeting of the Materials Research Society, Reno, NV, April 5-8, 1988.

Symposium K: High-Temperature Superconductivity

INVITED TALK

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INTRODUCTION

Neutron powder diffraction techniques have been used extensively for the study of high- T_c oxide superconductors because of the need to locate oxygen atoms and accurately determine the oxygen site occupancies, and the difficulty in obtaining single crystals. For example, in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, neutron powder diffraction and Rietveld structural refinement were used to obtain the first complete structural information. Subsequent experiments focussed on determining the relationship of superconducting properties to the number and distribution of oxygen vacancies on the Cu-O sublattice with measurements being done on samples in thermodynamic equilibrium, at high temperature in controlled oxygen atmospheres, and on metastable, oxygen-deficient samples produced by quenching. Neutron powder diffraction has also been used to determine the structures of compounds in which the properties have been modified by substitution on the Y, Ba, or Cu sites. This paper briefly reviews some of the neutron powder diffraction results in these areas.

OXYGEN-DEFICIENT $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

Following the initial discovery of an orthorhombic-to-tetragonal (O-T) transition at high temperature in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, a series of neutron diffraction experiments were done in order to learn the relationship between the structural transition and the formation of oxygen vacancies on the Cu-O sublattice and to correlate the superconducting and structural properties of oxygen-deficient samples. Extensive *in situ* neutron diffraction measurements were made as a function of temperature and oxygen partial pressure and compared with results for samples quenched into liquid nitrogen from the same regions of the high-temperature phase diagram. In the first *in situ* experiment, $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ was studied at temperatures from 400 C to 950 C at constant oxygen partial pressures of 1, 0.2, and 0.02 atm.[1] The results suggested that it should be possible to produce metastable, oxygen-deficient samples covering a range of oxygen concentrations and to study the relationship between superconducting and structural properties. Suitable samples were produced by quenching into liquid nitrogen from temperatures ranging from 400 C to 950 C at 1 atm. of oxygen.[2,3] These initial results were then extended by performing

*Work supported by the U. S. Department of Energy, Basic Energy Sciences - Materials Sciences, under contract number W-31-109-ENG-38.

measurements at constant temperature as a function of oxygen partial pressure. *In situ* measurements spanned the oxygen partial pressure range from 1 atm. to 2×10^{-4} atm. at 490 C and 440 C [4] and were compared with results for samples quenched from 500 C for the same range of partial pressures.[5]

A number of conclusions can be drawn from these experiments. The O-T transition results from the combined effects of the loss of oxygen from the structure and the movement of oxygen atoms from originally occupied sites to originally vacant sites. As the temperature is increased or the oxygen partial pressure lowered, vacancies are formed on the (0,1/2,0) oxygen sites, disrupting the one-dimensional chains which are a unique feature of the stoichiometric, $T_c=90$ K, ($\delta \approx 0$) compound. At the same time, but at a slower rate, oxygen atoms occupy the originally vacant (1/2,0,0) sites between the chains. In thermodynamic equilibrium, these decreasing and increasing occupancies meet at a value of 0.25 for each site (i.e., a total basal plane occupancy of 0.5 for the two sites) resulting in a second order transition to the tetragonal phase. The temperature of this transition varies from 700 C at 1 atm. to 490 C at 1.5×10^{-3} atm. Additional vacancies are observed to form on the (0,0,z) oxygen site in the low-partial-pressure region of the phase diagram. Thus, even though the transition always occurs at a basal plane occupancy of 0.5, the total oxygen stoichiometry at the transition varies from 6.5 at 1 atm. to about 6.4 at 10^{-3} atm.

Quenched samples exhibit many structural similarities to *in situ* samples and some important differences. Vacancies appear only on the (0,1/2,0), (1/2,0,0) and (0,0,z) oxygen sites. However, the total oxygen content and distribution of vacancies does not accurately mimic that which exists at the equilibrium conditions prior to quenching. This results in an apparent shift of the O-T transition to higher temperatures or lower oxygen partial pressures, thus, effectively extending the orthorhombic region of the phase diagram. Additionally, some of the structural data for metastable, quenched samples suggest that, in this case, the O-T transition can occur at a basal plane occupancy lower than the value of 0.5 which is always observed in thermodynamic equilibrium. It is not clear whether these differences are intrinsic or simply artifacts of this particular quenching process.

COMPOUNDS OF THE FORM $RE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$

Shortly after the discovery of superconductivity in $YBa_2Cu_3O_{7-\delta}$, it was shown that isostructural compounds could be formed with a number of other rare earth ions on the Y site. Even in the case of magnetic rare earths, these compounds exhibited superconductivity with T_c near 90 K. It was observed, however, that substitution on the Ba site usually lowered T_c and produced a more pronounced effect on the crystal structure.[6] In this context, a family of compounds which exhibit interesting superconducting and structural behavior are those with the formula $RE_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$. In

this case a rare earth ion (RE) fully substitutes the Y site and also partially substitutes the Ba site. The first of these compounds to receive attention was $\text{La}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$, in which it was observed that the properties could be varied from superconducting to insulating by varying x . For $x=0$, this compound is isostructural with orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and is a superconductor with T_c approaching 90 K, while for $x=0.5$, the compound is isostructural with tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, with random occupancy of 25% La and 75% Ba on the Ba site, and is an insulator.[7-10] Neutron diffraction studies showed that the transition from orthorhombic to tetragonal symmetry was a result of the substitution on the Ba site and not a result of the formation of oxygen vacancies, as in the case of oxygen deficient $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. [9,10] In fact, the overall oxygen stoichiometry was observed to increase above 7 with increasing x . Experiments which attempt to accurately determine the values of x where the structural transition occurs and where T_c reaches zero have been hampered by difficulties in synthesizing homogeneous samples and by the fact that the dependence of T_c on oxygen deficiency is far more pronounced than in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. [11]

Other compounds of the form $\text{RE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7-\delta}$, however, have been shown to be easier to synthesize over the desired range of $0 < x < 0.5$. The solubility limits for $\text{RE}=\text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{and Dy}$ have been reported by Zhang et al. [12] Among these rare earths, Nd appears to be a good candidate for the study of the relationship between superconductivity and structure in this family of compounds. Initial neutron diffraction studies suggest that the orthorhombic-to-tetragonal structural transition occurs near $x=0.2$, while T_c reaches zero near $x=0.35$. [13]

COMPOUNDS OF THE FORM $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$

A second set of compounds which have received considerable attention are those in which an attempt has been made to substitute on the Cu site. A considerable amount of literature now exists reporting Cu-site substitution by Al, Co, Fe, Ga, Mn, Ni, and Zn and describing the effects on the superconducting properties. Even though many authors speculate on the effect of the dopant based on the assumption that either the Cu1 or Cu2 site in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is being substituted, in only a few cases has the location of the M ion in the crystal structure actually been determined by diffraction methods. The ability to locate the dopant ion depends, of course, on the contrast provided by the scattering cross sections. Al has been shown to substitute for Cu1 by single crystal x-ray diffraction. [14] Co has been shown to also substitute for Cu1 by two independent neutron diffraction experiments. [15,16] However, recent neutron diffraction experiments for samples of starting composition $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{7-\delta}$ show that (if the defect is assumed to be substitutional) most of the Fe actually substitutes on the Ba site, with only a minor contribution on Cu2. [17] These results clearly demonstrate that one cannot safely assume the structure of defected $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ compounds without performing

diffraction measurements to confirm the location of the dopant ion. Moreover, defects which involve interstitial rather than substitutional sites should not be ruled out without investigation. Forthcoming neutron diffraction experiments will undoubtedly play a major role in the interpretation of data for the superconducting properties of compounds of the form $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-\delta}$.

REFERENCES

1. J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).
2. J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki, and A. P. Paulikas, *Phys. Rev. B* **36**, 5731 (1987).
3. W. K. Kwok, G. W. Crabtree, A. Umezawa, B. W. Veal, J. D. Jorgensen, S. K. Malik, L. J. Nowicki, A. P. Paulikas, and L. Nunez, *Phys. Rev. B* **37**, 106 (1988).
4. J. D. Jorgensen, H. Shaked, B. Dabrowski, and D. G. Hinks, (unpublished).
5. B. W. Veal, G. W. Crabtree, H. Claus, J. D. Jorgensen, L. J. Nowicki, A. P. Paulikas, W. K. Kwok, L. H. Nunez, and A. Umezawa, (unpublished).
6. B. W. Veal, W. K. Kwok, A. Umezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Paulikas, and C. H. Sowers, *Appl. Phys. Lett.* **51**, 279 (1987).
7. A. Maeda, T. Yabe, K. Uchinokura, and S. Tanaka, *Jpn. J. Appl. Phys.* **26**, L1368 (1987).
8. F. Izumi, H. Asano, T. Ishigaki, E. Takayama-Muromachi, Y. Matsui, and Y. Uchida, *Jpn. J. Appl. Phys.* **26**, L1153 (1987).
9. W. I. F. David, W. T. A. Harrison, R. M. Ibberson, M. T. Weller, J. R. Grasmeder, and P. Lanchester, *Nature* **328**, 328 (1987).
10. C. U. Segre, B. Dabrowski, D. G. Hinks, K. Zhang, J. D. Jorgensen, M. A. Beno, and I. K. Schuller, *Nature* **329**, 227 (1987).
11. E. Takayama-Muromachi, Y. Uchida, A. Fujimori, and K. Kato, *Jpn. J. Appl. Phys.* (in press).
12. K. Zhang, B. Dabrowski, C. U. Segre, D. G. Hinks, I. K. Schuller, J. D. Jorgensen, and M. Slaski, *J. Phys. C: Solid State Phys.* **20**, L935 (1987).
13. C. U. Segre, B. Dabrowski, D. G. Hinks, and J. D. Jorgensen (unpublished).
14. T. Siegrist, L. F. Schneemeyer, J. V. Wasczak, N. P. Singh, R. L. Opila, B. Batlogg, L. W. Rupp, and D. W. Murphy, *Phys. Rev. B* **36**, 8365 (1987).
15. T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono, and M. Hirabayashi, *Jpn. J. Appl. Phys.* **26**, L1727 (1987).
16. P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella, and J. D. Jorgensen, *Phys. Rev. B* (in press).
17. B. D. Dunlap, J. D. Jorgensen, W. K. Kwok, C. W. Kimball, J. L. Matykievicz, H. Lee, and C. U. Segre, *Proceedings of the International Conference on High-Temperature Superconductors and Materials and Mechanisms of Superconductivity, Interlaken, Switzerland, Feb. 29 - Mar. 4, 1988 (North-Holland, Amsterdam, in press).*