THE ABSENCE OF Y/Cu CATION DISORDERING IN $YBa_2Cu_3O_x$ *

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Summary

X-ray powder diffraction data obtained from $HoBa_2Cu_3O_x$ are examined to address the question of possible R/Cu antisite disorder in the $R1:2:3O_x$ 92 K superconductors. This disordering has been postulated based on analyses of Cu *K*-edge XANES data from $Y1:2:3O_x$. We find no evidence for Ho/Cu disorder, but instead find that a structural model assuming cation ordering best fits the data. We present chemical and structural arguments against antisite disorder in any of the $R1:2:3O_x$ compounds.

1. Introduction

The atomic structure of the high T_c superconducting oxide $YBa_2Cu_3O_x$ (Y1:2:3) has been extensively investigated by X-ray and neutron diffraction studies [1, 2], and found to be a distorted perovskite. Yttrium and barium order on the A site to cause a tripling of the basic perovskite cell in the c direction, while oxygen vacancy ordering results in two crystallographically inequivalent B sites for the copper atoms. The reported structures all include an ordering of yttrium and copper onto crystallographically different sites. It has recently been pointed out that neither X-ray nor neutron diffraction data are able to distinguish easily between yttrium and copper scattering, and would therefore be insensitive to a disordering of these two ions in the 1:2:3 structure [3, 4]. Using an unconventional method for the analysis of Cu *K* edge spectra (X-ray absorption near-edge spectroscopy (XANES)), evidence has been reported [3] for substantial (20 - 30%) disordering of yttrium and copper in $YBa_2Cu_3O_x$. Since the implications of such an antisite disorder would be far-reaching in terms of understanding the mechanism responsible for superconductivity at such a high temperature, we have set out to investigate this proposed Y/Cu cation interchange.

The difficulties found in X-ray or neutron diffraction data analysis arise from the similar scattering power of yttrium and copper and, in the case of X-ray data analysis, can be overcome by substitution of yttrium with a rare earth ion. Rare earths have much higher atomic numbers (62 - 68) than either yttrium (39) or copper (29), and possess substantially larger X-ray scattering powers. Most rare earth ions form superconducting compounds which are isostructural with $YBa_2Cu_3O_x$, and could be used for this comparison. We have chosen, for several reasons, to examine the X-ray powder pattern of $HoBa_2Cu_3O_x$. Most important is that the superconducting critical temperature T_c of Ho1:2:3, 92(1) K, is the same as that of Y1:2:3 [5]. The lattice constants and atomic coordinates are identical to within statistical error, reflecting the fact that both ions are trivalent and have similar ionic radii (see Table 1). Since it is known that the chemical reactions of yttrium and holmium are similar, and since there is little distinguishable difference between the structures or bulk properties of Y1:2:3 and Ho1:2:3, it is assumed that any disordering present for yttrium and copper would also occur for holmium and copper. For these reasons we can use X-ray diffraction data from $HoBa_2Cu_3O_x$ to investigate the Y/Cu antisite disordering model which has been proposed from XANES data [3, 4]. We present the results of this study below.

TABLE 1

Relevant constants for neutron scattering and X-ray scattering

	Cu	Y	Ho
Neutron scattering lengths (barns)	0.770	0.775	0.85
X-ray form factors at 50°, 2θ for Cu radiation $(\sin \theta/\lambda) = 0.28$	20.589	27.263	50.375
Atomic number	29	39	67
Ionic radius (Å) [6] VI coordinate	0.73	0.900	0.901
VIII coordinate	—	1.019	1.015

2. Experimental details

The samples were prepared by intimate mixing of stoichiometric amounts of Ho_2O_3, $BaCO_3$ and CuO, and firing to 975 °C. These mixtures were then reground, refired in oxygen and furnace cooled. X-ray powder patterns were obtained using a Scintag PADV theta–theta diffractometer using Cu $K\alpha$ radiation, and calibrated against a National Bureau of Standards silicon standard.

3. Results

The cell parameters obtained from the X-ray powder pattern of $HoBa_2Cu_3O_x$ agree well with those reported previously from an analysis of neutron diffraction data [5]. The peak intensities were extracted by fitting to a gaussian line shape(s) with variable line width. For multiple peaks with peak maxima closer than 1.5 times the width at half-height, an integrated intensity was used. Only peaks with intensities greater than 1% of the maximum peak counts were included in this analysis. In addition, only data in the range $10 \leqslant 2\theta \leqslant 60$ were used in an effort to minimize errors resulting from variations in thermal effects, line overlap and line splitting arising from the separation of Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation.

These experimental data were compared with a series of model calculations. Model intensities were obtained from computer simulations using *LAZY PULVERIX* [6] with positional and thermal parameters taken from ref. 1. The various models are identical except for the varying degrees of Ho–Cu2 antisite disorder (Cu2 is the "plane" copper, as defined in ref. 1). The experimental intensities, together with those predicted for various degrees of antisite disordering, are listed in Table 2.

In order to estimate how well a model is able to reproduce the experimental data, agreement factors R are calculated according to

TABLE 2

The experimental X-ray intensities together with intensities calculated assuming 0%, 5%, and 30% Ho/Cu antisite disordering

	Experimental data	0%	5%	30%
001	7.3	7.8	8.1	8.5
003/010[a]	18.7	13.6	12.1	6.9
100[a]	5.2	5.2	3.8	1.8
012	2.0	0.7	0.9	1.1
102	3.1	1.9	1.9	2.1
013	46.9	45.4	45.1	45.1
103/110	100	100	100	100
112	<0.5	0.6	0.75	0.87
005/014	16.7	7.8	8.0	8.5
104[a]	5.2	3.1	3.2	3.4
113[a]	16.7	15.9	14.7	10.5
006/020	29.2	23.2	23.0	22.8
200	10.4	13.9	13.9	13.8
115	3.1	1.9	2.0	2.3
016	1.0	1.4	1.3	0.80
023[a]	2.0	1.6	1.3	0.80
106[a]	2.0	1.1	0.94	0.58
116/123	33.3	34.1	34.0	33.6

[a]Reflections used to determine R_{part}.

TABLE 3

Various agreement factors for different models as outlined in the text

Substitution (%)	R_{full}	R_{part}	R_{cf}
0.0	9.4	14.1	0.0
5.0	—	17.3	2.6
10.0	—	19.8	5.5
30.0	14.5	32.4	15.9

$$R = \frac{\Sigma(I_o - sI_c)}{\Sigma I_o} \qquad (1)$$

where I_o and I_c are the observed and calculated intensities and s is the scale. The only variable parameter in this comparison is the scale, which is minimized for every R.

Table 3 lists three different R values. The first, R_{full}, is a comparison of all experimentally observed reflections ($I_o > 1\%$) with the corresponding model intensities. The results of these calculations for the 0% and 30% cases, shown in Table 3, reveal that the fully ordered structure gives a better agreement factor (9.4%) than does the 30%-disorder model (14.5%). This result indicates that, if there is any antisite disorder, it is less than the 30% predicted from XANES data. In order to distinguish more precisely the degree of antisite disorder, another agreement factor was calculated. From a comparison of the intensities of calculated reflections as a function of per cent disorder, it was noted that some reflections are far more sensitive than others to changes in the models. In particular, the intensities of six reflections change significantly with the degree of disorder. Using only these six reflections, an agreement factor R_{part} was calculated to determine an upper limit to the possible degree of disorder. A comparison was made between experimental data on models calculated assuming 0, 2, 5, 10, 20, 30 and 40% disordering of holmium and Cu2, with the scale as the only variable parameter. It is clear from Table 3 that the model with no disordering best represents the experimental data.

The third agreement factor R_{cf} is a comparison of the 0% disorder model I_o with the other models I_c, *i.e.* no experimental data are included in this comparison. It represents the statistical difference between the various models, and has been used to help in judging the upper limit to the Ho/Cu2 disorder possible. As seen from Table 3, there is a linear increase in R_{cf} with per cent disordering, which is also observed in R_{part}, indicating that the difference in R_{part} between no Ho/Cu2 disorder and 2% antisite occupation is significant. In fact, our data analysis indicates that there is *less than* 2% disordering of the holmium and Cu2, the statistical limit of our experiment.

There is no significant disordering of the copper onto the rare earth site and vice versa. Recent X-ray and neutron diffraction data on Y1:2:3 also support our findings [2, 7]. In addition to diffraction results, there are

several independent indications which point to a total ordering of these ions. Firstly, from a chemical viewpoint, it is very unlikely that yttrium and copper would disorder. Their ionic radii (listed in Table 1) are substantially different, with the larger yttrium ion preferring the larger coordination number. Furthermore, if yttrium and copper were able to disorder, then it should be possible to form solid solutions extending away from the 1:3 stoichiometry. In other words, there should be a line of compounds on the Y–Ba–Cu phase diagram corresponding to the series $Y_{1-x}Ba_2Cu_{3+x}O_7$ where x would be a small negative or positive number. Such a phase line does not exist [8, 9]. In addition, ^{155}Gd Mössbauer data obtained on the isostructural compound $GdBa_2Cu_3O_x$ [10] show evidence of only one site, not the two which would be present if gadolinium were to disorder onto the Cu2 site.

4. Conclusions

The X-ray diffraction results presented here on $HoBa_2Cu_3O_x$ rule out any substantial Ho/Cu antisite disorder. The ordering of the lanthanide and copper on crystallographically inequivalent sites is also supported by other chemical and spectroscopic data. Based on the chemical similarities of yttrium and the other rare earths, as well as the similarities in lattice constants and critical temperatures of $RBa_2Cu_3O_x$, where $R \equiv Y$ or a lanthanide, we argue that our results on Ho1:2:3 can be extrapolated to Y1:2:3. In this case, the results presented here do not agree with the structural model proposed from XANES and extended X-ray absorption fine structure data.

Acknowledgements

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