A systematic neutron diffraction study of RBa2Cu3O7 (R = yttrium and rare earths) high-Tc superconductors

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Abstract

The 10 K crystal structures of high-T_c RBa$_2$Cu$_3$O$_7$ (R = Y and rare earths) ceramic materials investigated by neutron diffraction were consistently analysed concerning systematic trends. Several interionic distances exhibit the well known lanthanide contraction behaviour, i. e., a linear relationship with the ionic radii of trivalent rare-earth ions. The only exceptions are associated with the apex oxygen O(1) ions: the chain copper Cu(1)-O(1) distances are constant, and the plane copper Cu(2)-O(1) distances are increasing across the rare-earth series. For R = Pr the 4f-CuO$_2$ valence band hybridization effects are found to be highly anisotropic, since exclusively the interionic distances involving the b-direction (i. e., the chain direction) indicate that the Pr ions have an intermediate valence of about +3.4.

1. Introduction

The crystal structure, i. e., the arrangement of atoms in a material, largely determines its physical properties. Crystal structure determination is then one of the basic requirements for any new substance. This is particularly true for the high-T_c perovskite-type compounds whose superconducting properties are strongly related to the structural details. The real structural question for these compounds has been to elucidate details of the oxygen coordination such as the important features of the puckered copper-oxide planes, various copper-oxide bond lengths, etc. Neutron powder diffraction has repeatedly proven to be especially useful for such problems because of the sensitivity for light atoms such as oxygen.

It is the purpose of the present work to provide a consistent set of structural parameters for the compounds RBa$_2$Cu$_3$O$_7$ (R = Y, La, Pr, Nd, Sm, Dy, Ho, Er, Tm, Yb). In order to get a systematic insight into the structural behaviour of the rare-earth series it is necessary to perform low-temperature neutron diffraction experiments on samples prepared with the same procedure and analysed under identical conditions. So we present here for the first time an internally consistent structural analysis of most rare-earth high-T_c compounds of the "123" perovskite type.

2. Experimental procedures and results

The polycrystalline samples of RBa$_2$Cu$_3$O$_7$ (Fig. 1) were prepared at our laboratory by a standard sintering procedure as described by Rupp et. al. [1] with the exception of the R = Pr, Dy and Yb samples which were prepared at the Asea Brown Boveri Research Laboratory at Baden (Switzerland). The data for R = Y and R = Sm are taken from Refs. [2] and [3], respectively.
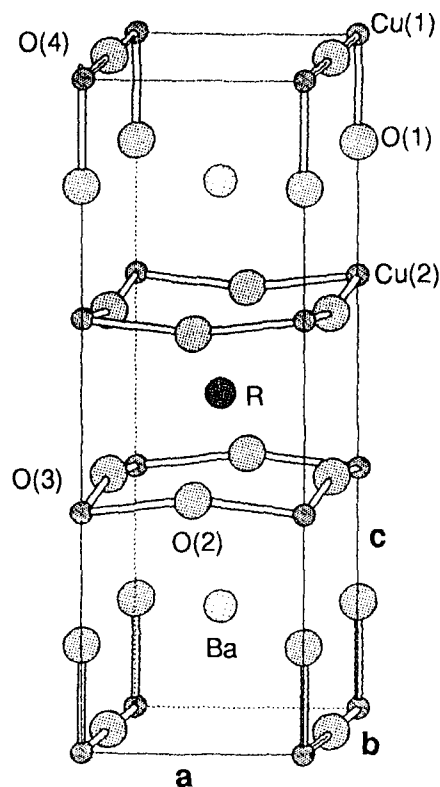

Figure 1. Orthorhombic RBa$_2$Cu$_3$O$_7$ (R = Y and rare-earth) structure.

The neutron diffraction data were collected at T = 10 K with use of the multidetector powder diffractometer DMC [4] in the high resolution mode at the reactor SAPHIR in Würenlingen, Switzerland (liquid-nitrogen-cooled Si filter, vertically focussing Ge (311) monochromator , collimation 10'/ - /12', wavelength 1.7012(5) Å). The diffraction patterns were refined employing the Rietveld method using a modified program version by Wiles and Young [5].

The detailed structural parameters have been published in Ref. [6]. Here we discuss various interionic distances in relation to the radii for trivalent R ions.

3. Discussion of results

The cell parameters a, b and c/3 (Fig. 2) clearly show the expected lanthanide contraction behaviour, i. e., they exhibit a perfectly linear relationship when plotted versus the ionic radii for trivalent rare-earth ions [7], with two exceptions. Firstly, for the Pr ion we infer a valence intermediate between +3 and +4 from the cell parameter c, whereas a trivalent character results from the cell parameters a and b. Secondly, the La sample shows a rather tetragonal structure with an orthorhombicity (b-a)/(b+a) = 0.22% which is much smaller than for the other samples [6], where the orthorhombicity is about 0.80%. Moreover, our data analysis for R = La yields an O(5) occupation of n[O(5)] = 0.3 and a mixed site occupation of Ba^{2+} (about 15%) and La^{3+}.
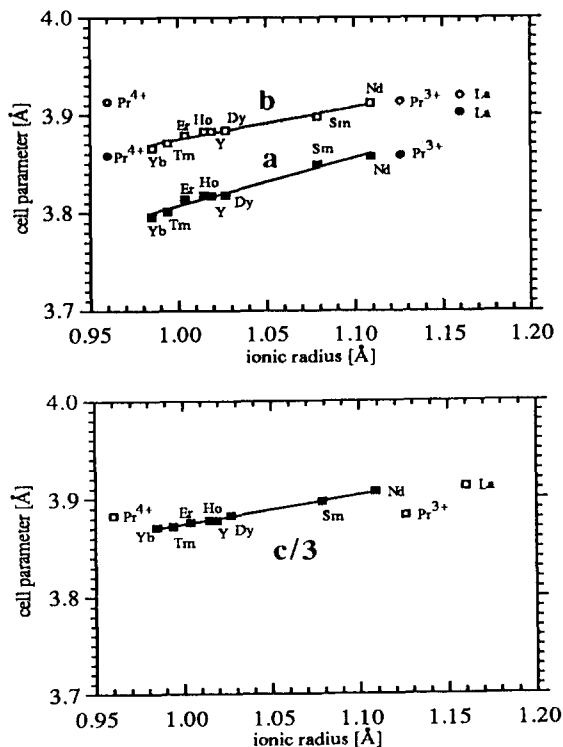

Figure 2. Lattice parameters a,b and c/3 of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

We now proceed to discuss in detail some relevant interatomic distances which are found to scale perfectly with the ionic radii for trivalent rare-earth ions as will be shown below. In all the subsequent figures this linear relationship is indicated by a straight line fitted to the data. The La and Pr compounds are excluded from this fit.

Fig. 3 shows the CuO_2 plane separations, i. e., the distances Cu(2)-Cu(2), which are particularly sensitive to the lanthanide contraction, since the rare-earth ions are situated between the CuO_2 planes. In fact, the Cu(2)-Cu(2) distances are found to contract twice as much as does the lattice parameter c across the rare-earth series. For Pr we find an intermediate valence of +3.4 by interpolation.
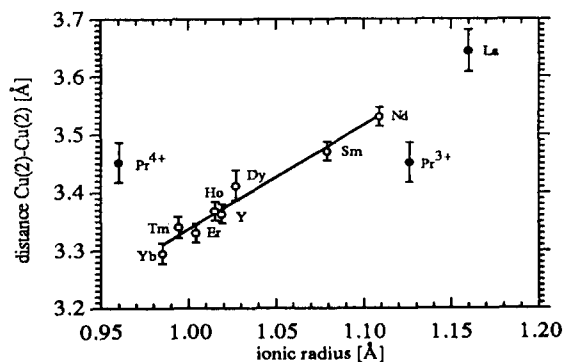

Figure 3. Distance Cu(2)-Cu(2) of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

As shown in Fig. 4 the distance between the plane copper Cu(2) and the apical oxygen O(1) increases linearly from the light to the heavy rare-earth compounds. The bond Cu(2)-O(1) in the deoxygenated $RBa_2Cu_3O_x$ samples is strongly related to the superconducting transition temperature T_c which has been attributed to charge transfer effects [8]. However, the small variation of T_c across the rare-earth series (T_c = 94 K for R = Nd, T_c = 90 K for R = Yb) can probably not be related to the observed behaviour of the Cu(2)-O(1) bond length.
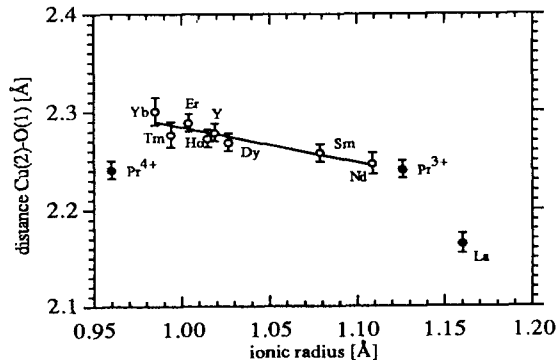

Figure 4. Distance Cu(2)-O(1) of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

The distance between the chain copper Cu(1) and the O(1) apex atom (Fig. 5) is constant for the whole rare-earth series, as already found by Neumeier et. al. [9] for $Y_{1-y}Pr_yBa_2Cu_3O_7$. The Cu(1)-O(1) distance has often been taken as a measure of the chain site copper valence, however, even for the intermediate valent Pr compound there is no charge transfer to the chains.
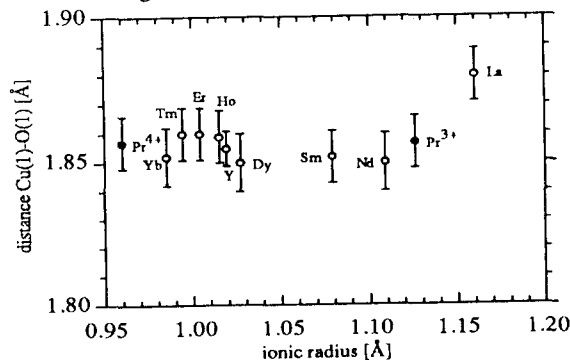

Figure 5. Distance Cu(1)-O(1) of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

Concerning the distances between the rare-earth and the plane oxygen ions we find slightly larger values for R-O(2) than for R-O(3) (Fig. 6). Most interestingly, the distance R-O(3) is clearly compatible with Pr^{3+}, whereas from the distance R-O(2) we again derive a Pr valence of +3.4. Obviously the hybridization between the Pr ion and the plane oxygen is exclusively associated with the O(2) ions, i. e., it acts along the b chain direction.
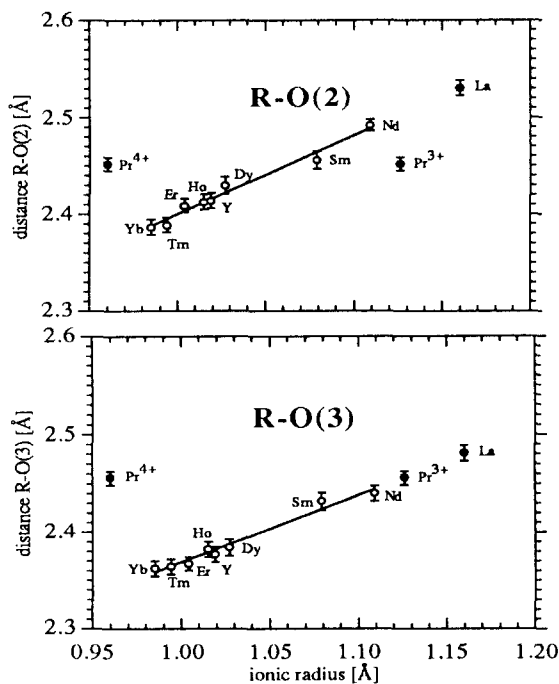

Figure 6. Distances R-O(2,3) of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

Similar results evolve from a comparison of the in-plane distances Cu(2)-O(2) and Cu(2)-O(3) as shown in Fig. 7. While the bond length Cu(2)-O(2) is compatible with trivalent Pr ions, we derive an intermediate Pr valence of+3.4 from the distance Cu(2)-O(3), which is again lying along the b chain direction.
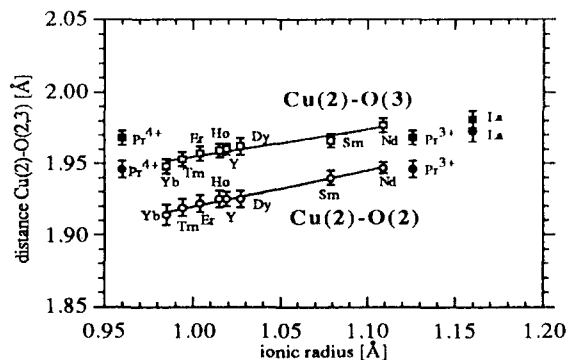

Figure 7. Distances Cu(2)-O(3) and Cu(2)-O(2) of $RBa_2Cu_3O_x$ versus radius of trivalent R ions.

4. Conclusions

We have presented a consistent set of structural data for the high-T_c $RBa_2Cu_3O_x$ compounds and analysed the results with respect to systematic trends. The lattice parameters and a large number of interionic distances are found to scale linearly with the ionic radii of trivalent rare-earth ions. By interpolation we find that the Pr ions in $PrBa_2Cu_3O_7$ have an intermediate valence of +3.4, which is comparable to the value of +3.3 derived by Neumeier et. al. [7] from $Y_{1-y}Pr_yBa_2Cu_3O_7$ structural data. The excess charge on the Pr ions, compared to the other rare-earth counterparts, results directly in a reduction of the hole concentration in the CuO_2 planes of $PrBa_2Cu_3O_7$ and thereby in a complete loss of the superconductivity. Our results indicate that the Pr 4f-CuO_2 valence band hybridization effects are strongly anisotropic and occur predominantly along the b chain direction. The strong hybridization of the Pr-O(2) bond along the b-axis may be the reason for the unusually high Néel temperature of about 17 K [10] associated with the Pr sublattice, which exceeds the values of T_N observed for the other $RBa_2Cu_3O_7$ compounds by roughly an order of magnitude. The hybridization leads to partial delocalization of the 4f electrons which manifests itself in drastically enhanced linewidths of crystal-field transitions as observed in neutron spectroscopic investigatons of $PrBa_2Cu_3O_7$ [11].

Similar neutron diffraction studies of the tetragonal $RBa_2Cu_3O_6$ series are presently being carried out. A

preliminary analysis for $PrBa_2Cu_3O_6$ indicates a perfectly trivalent character of the Pr ions.

Acknowledgments

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