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Neutron diffraction study of anisotropy of crystal lattice compression in high-T_c superconductors under pressure

V. Voronin, A. Mirmelstein, A. Karkin, A. Teplykh, and B. Goshchitskii

Institute for Metal Physics, Russian Academy of Sciences, 18, S. Kovalevskaia str., 620219, Ekaterinburg GSP-170, Russia

A. Ivanov

Vereshchagin High Pressure Physics Institute, 132092 Troitsk, Moscow region, Russia

L. Smirnov

Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Moscow region, Russia

Pressure-induced structural changes in irradiated $YBa_2Cu_3O_x$ (x = 6.95) and unirradiated (x = 6.91, 6.54, 6.39) samples have been measured by neutron powder diffraction under high pressure. T_c has been measured for irradiated superconductors under pressure and the value of dT_c/dP is found to be high (1.5 K/kbar). The increase in T_c is associated with charge transfer between the CuO_2 planes and CuO chains which is reflected by anisotropy of crystal lattice compression.

It is common knowledge that high-T_c superconductivity is caused by a charge state of the CuO_2 plane which is determined by a charge transfer between this plane and the reservoir. Since HTSCs are ionic compounds, it is possible to determine atomic valences in a cell using the cation-anion bounding lengths [1]. With this method Cava [2] calculated cation valences in $YBa_2Cu_3O_x$ for different x using structural parameters derived from neutron diffraction studies, and showed that with increasing oxygen concentration and T_c, respectively, charge transfer to the CuO_2 plane from the CuO chains, as charge reservoirs, is observed. It is accompanied by a marked increase in the lattice parameter c unlike a and b, i.e., by anispotropic lattice expansion. As a result of the $YBa_2Cu_3O_x$ anisotropic lattice compression under pressure and, consequently, of a charge transfer from the CuO chains to the CuO_2 plane, the superconducting transition temperature increases [3]. Thus, anisotropy of lattice expansion or compression is a manifestation of a charge transfer between the planes which affects the T_c. However, crystal lattice expansion with constant oxygen concentration in a cell under radiation-induced fast neutron disordering of the $YBa_2Cu_3O_x$ samples results in strong T_c degradation [4]. So, it was of interest to study variation of T_c and lattice of the radiation disordered $YBa_2Cu_3O_x$ under conditions of overall compression, since in this case the volume of a cell decreases, being an opposite event against lattice expansion under disordering. We have carried out a neutron diffraction study of the variation in the structure of the radiation — disordered ceramic $YBa_2Cu_3O_{6.9}$ samples under hydrostatic high pressure. These measurements were carried out with the help of a high pressure cell [5]. The samples were irradiated by fast neutron fluences 2 and $5 \cdot 10^{18}$ cm^{-2} under liquid nitrogen temperature (80 K) and heated to room temperature. For comparison, we also carried out structural studies on the influence of pressure on the structure of unirradiated $YBa_2Cu_3O_x$ samples with different x. The neutron diffraction patterns were treated by the Rietveld method using the program «Fullprof» [6].

Figure 1 demonstrates a typical pattern treated by Rietveld method for $YBa_2Cu_3O_x$ (x = 6.54, P = = 5.7 kbar). Structural parameters (parameters of the crystal lattice, atomic positions, oxygen occupations) for the radiation disordered samples investigated under different hydrostatic pressure were published previously in [7]. We obtained strong and different dependence of a, b and c parameters, i.e. a strong compression anisotropy [8–10], on composition and fluence (see Table 1). The strongest dif-

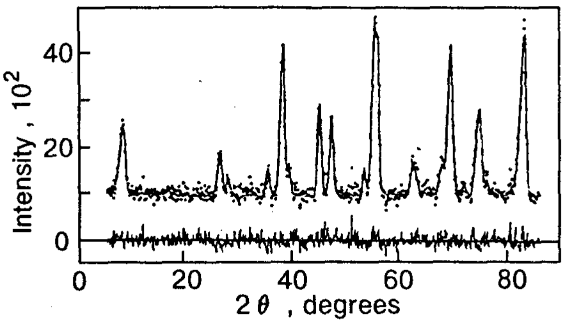

Fig. 1. Observed, calculated and difference neutron diffraction patterns of $YBa_2Cu_3O_x$ (x = 6.54, P = 5.7 kbar).

ference in compression factors is observed along the c axis.

Table 1

Coefficients of linear and volume compression for $YBa_2Cu_3O_x$

x	Fluence, 10^{18} cm^{-2}	k_a	k_b	k_c	k_V
		10^{-3} Å/kbar			
6.91	0	0.20	0.18	0.40	0.80
6.54	0	0.24	0.21	0.59	1.03
6.39	0	0.25	0.23	0.65	1.20
6.91	2	0.29	0.32	0.44	1.03
6.91	5	0.37	0.42	0.55	1.38

We describe the resultant complex dependences of lattice parameters on the oxygen concentration, radiation and high pressure as the dependence of the differences $\Delta\sqrt{ab} = \sqrt{a_i b_i} - \sqrt{a_j b_j}$ on $\Delta(c/3) = (c_i/3) - (c_j/3)$ where a_i, b_i and c_i are the initial parameters a, b and c in the $YBa_2Cu_3O_x$ samples and

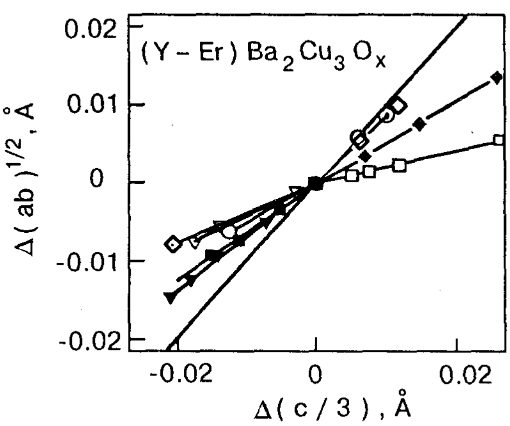

Fig. 2. $\Delta(ab)^{1/2}$ vs. $\Delta(c/3)$. For different x (□), fluences F [○, ◇ (x = 6.9), ◆ (x = 6.18)] . For different pressure in unirradiated (○, ∇, ◇) and irradiated for F, 10^{18} cm^{-2}: 2 (■); 5 (▼).

a_j, b_j and c_j are varied parameters of the samples subject to any influence. Essentially different slopes of the curves correspond to different lattice expansion anisotropy under irradiation and with decreasing x from 7 to 6 (Fig. 2) as well as to compression anisotropy of irradiated and unirradiated oxygen-deficient samples under pressure (Fig. 2).

This anisotropy is likely to indicate a different value of charge transfer along the c axis. Let us try to evaluate charge variation under pressure according to the above method. Using the bond lengths derived from the experimental structural parameters [7] we calculated cation valences of Y, Ba and the in- and out-of-plane contributions Cu1p, Cu2p, Cu1c, Cu2c, respectively, to the total bond valence sum Cu1, Cu2 for all the samples under study. We differentiated the contributions of the apical oxygen (Cu-O along the c axis) and oxygen atoms which lie in the CuO_2 and CuO planes to copper valence.

The value of these contributions depends on the lattice compression anisotropy and atomic coordinates, being responsible thus for variation of interatomic distances. The irradiated samples formal increase in the valence of the Cu2 atoms is connected only with increasing oxygen contribution in the CuO_2 plane while in unirradiated samples this increase is determined by both the contributions.

Under compression the total charge of the whole cell is formally increased. Actually this is not the case. Of course, the total charge remains constant. To take into account this unvariability of the cell charge we may correct constant values of r_0 in the formula to keep the total charge [3]. It is clear that it decreases with decreasing the unit cell volume under compression. However, we know about the inverse process, when the lattice expands, with stoichiometry being unchanged. This is the case of fast neutron irradiation. Thus, on compression, irradiated samples have the same value of the total charge as the initial unirradiated sample. Hence, it is not necessary to change the value of constant r_0, which is a delicate enough task. In fact, for P = 6.4 kbar the total charge of the irradiated sample is the same as for unirradiated one without pressure (Table 2), their volumes are the same too.

Table 2

Bond valence sum and volumes vs. irradiation and pressure

P, kbar	F, 10^{18} cm^{-2}	Bond sum	V, Å^3
0	0	13.82	173.28
0	2	13.80	174.12
0	5	13.56	174.65
6.4	2	13.81	172.95
6.4	5	13.815	173.18

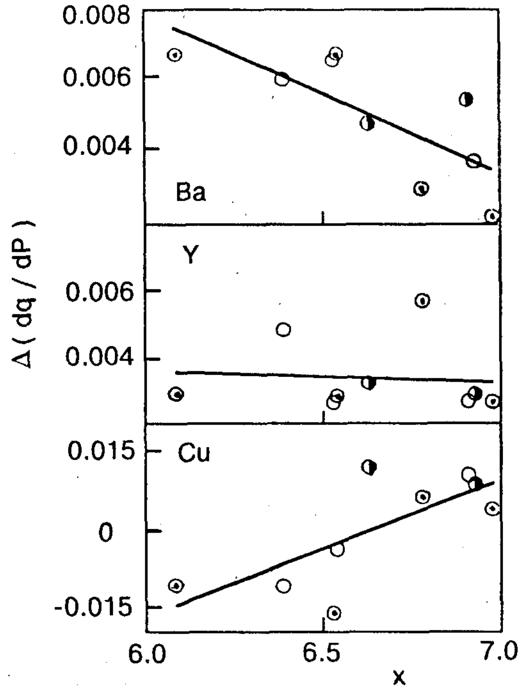

Fig. 3. Difference of dq/dP vs. oxygen content for $RBa_2Cu_3O_x$. O— [3]; O— [11]; O—our data.

Moreover, valences of the Y and Ba atoms also turned out to be equal to their initial values, while those of the copper atoms in the Cu1 and Cu2 sites differ from their initial values, thus allowing us to assume a charge redistribution. It was shown previously [9] that under irradiation there is no charge transfer between the planes. Hence, in this case we may compare the charges of Cu1 and Cu2 with those for the unirradiated sample. Their variation is seen to be 0.02/6.4 q/kbar corresponding to the value of 0.033/10 q/kbar obtained while investigating electrical crystalline field effects [11]. A more complicated case is presented by a compressed $YBa_2Cu_3O_x$ with different x. For $x = 6.9$ the value of the formal cation charges varied in the same way on compression and we may correct r_0 to keep the initial charge of a cell according to [3]. Thus, the valence of Cu2 increases by something of the order of 0.02/8 q/kbar, being comparable with that from the literature. However, on compression the samples with different x show large variations in copper valence obtained by this method. To compare our results with those from the literature we calculated all the valences and took the pressure derivative (dq/dP). To avoid the influence of the experimental conditions in Fig. 3 we show the difference of dq/dP vs. oxygen content with pressure and without it. For Y the value of dq/dP does not depend on composition whereas it does for Ba and Cu.

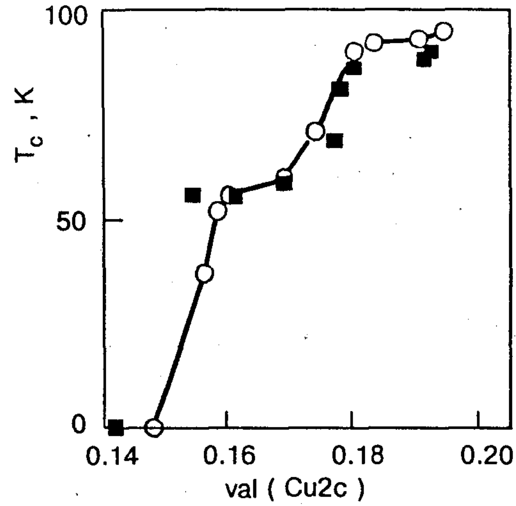

Fig. 4. T_c vs. contribution of apical O to the Cu2 valency: ■ — [2]; O — our data.

Hence, while evaluating the charge redistribution in the lattice we have to account for coordinate variations in the valence not only for the copper but also for the barium atoms. It is a complicated problem and we have not solved it as yet. Note that experiments on redistribution effects in $ErBa_2Cu_3O_x$ under pressure yield approximately the same value for charge transfer for all values of x [11].

We now compare the variation in the structure and T_c. It is known that variation of theCu2 valence correlates with T_c with decreasing x [2]. According to our experiments this variation is due to a contribution of the apical oxygen alone while the contribution of the in-plane atoms does not depend on x. The same result is obtained from the data of [2] where we differentiated between the contributions of the apical oxygen and the CuO_2 plane atoms to the total Cu2 valence. Hence, Fig. 4 shows T_c as a function of the apical oxygen contribution (x varying from 6 to 7), which demonstrates two plateaus for $x = 6.9$ and 6. 6.

From this curve it is easy to explain two peaks in the derivative dT_c/dP vs. oxygen content [12]: small changes in the valence of the Cu2 atoms under pressure result in a dramatic increase in T_c. According to our measurements of the superconducting transition temperature for radiation disordered samples, T_c increases with pressure (≈ 1.5 K/kbar), which also may be explained by charge transfer found under compression.

Conclusions

1. Anisotropy of the crystal lattice compression of radiation disordered $YBa_2Cu_3O_x$ under the influence of hydrostatic pressure has been found.

2. Charge transfer between the CuO_2 planes and CuO chains is demonstrated in radiation-disordered $YBa_2Cu_3O_x$ under pressure, accompanied by increasing T_c.

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