Neutron Scattering Study of Sr Substitution for Ba in $YBa_2Cu_3O_{7-y}$*

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Neutron diffraction and inelastic scattering were carried out on $YBa_{2-x}Sr_xCu_3O_{7-y}$ (x=0.5, 1.0, 1.25). It was confirmed that the substitution of Sr for Ba in $YBa_2Cu_3O_{7-y}$ increases the oxygen vacancies in the Cu–O chain. Moreover, the substitution strengthens the coupling between the Ba–O plane and the Cu–O chain, and reduces the crystal stability. These are the possible causes of T_c depression for Sr substituted $YBa_2Cu_3O_{7-y}$.

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Since the discovery of "123" high-T_c superconductor, there have been many studies of changes in the superconducting properties of that material induced by substitution for the original atomic species. Most of those studies have been concentrated on Cu or Y atoms. Recently, more attentions have been paied to the Ba–O plane, the bridge between Cu–O plane and Cu–O chain. But the study of Sr substitution for Ba is still rather limited and some conclusions are not agreeable.[1–5]

Veal *et al.*[3] found that the substitution of Sr for Ba yields a linear depression of T_c with the Sr concentration, which is attributed to the formation of oxygen vacancies in Cu–O chain as well as distortions in the neighborhood of the Ba(Sr) atoms. Zhao *et al.*[5] found that T_c changes with the content of Sr either monotonously or nonmonotonously, depending on the preparation condition. They inferred that monotonous depression of T_c results from oxygen vacancies formed on Ba–O plane which weakened the coupling between Cu–O plane and Cu–O chain. In order to make that clear and to find out the mechanism of Sr substitution effect further, we determined the crystallographic sites occupied by oxygen vacancies in $YBa_{2-x}Sr_xCu_3O_{7-y}$ (x=0.5, 1.0, 1.25) by powder neutron diffraction and deduced the generalized phonon density of states (GPDOS) from inelastic scattering measurements.

The samples of $YBa_{2-x}Sr_xCu_3O_{7-y}$ (x=0.5, 1.0, 1.25) were prepared under the same preparation conditions by mixing stoichiometric proportion of $BaCO_3$ ($SrCO_3$), Y_2O_3 and CuO, grinding, and twice preheating at 920°C in air for 24 h. Then, the reacted product was reground, pressed into pellets, sintered at 950°C in air for 48 h, and finally cooled down to room temperature in an oxygen atomsphere (1 atm). All of the three samples were identified to be of single phase with orthorhombic $YBa_2Cu_3O_{7-y}$ structure using x-ray diffraction. The standard

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resistive method was used to determine the superconducting transition temperature (T_c) which are listed in Table 1.

Table 1. Structural parameters of $YBa_{2-x}Sr_xCu_3O_{7-y}$.

		x=0.5		x=1.0		x=1.25	
		T_c=85 K		T_c=82 K		T_c=78 K	
		a=3.8095(15)		a=3.8019(15)		a=3.7970(21)	
		b=3.8739(16)		b=3.8539(17)		b=3.8471(23)	
		c=11.6364(54)		c=11.5765(53)		c=11.5296(69)	
Element	Site	z	n	z	n	z	n
Ba	2t	0.1846(7)	1.5	0.1834(7)	1.0	0.1821(9)	0.75
Sr	2t	0.1846(7)	0.5	0.1834(7)	1.0	0.1821(9)	1.25
Y	1h	0.5	1.0	0.5	1.0	0.5	1.0
Cu(1)	1a	0.0	1.0	0.0	1.0	0.0	1.0
Cu(2)	2q	0.3524(6)	2.0	0.3534(6)	2.0	0.3548(8)	2.0
O(4)	2q	0.1596(7)	2.0	0.1589(8)	2.0	0.1589(10)	2.0
O(2)	2s	0.3775(12)	1.88(4)	0.3795(13)	1.90(5)	0.3729(16)	1.90(6)
O(3)	2r	0.3775(13)	2.0	0.3782(14)	2.0	0.3799(17)	2.0
O(1)	1c	0.0	0.97(3)	0.0	0.84(3)	0.0	0.82(3)
O(5)	1b	0.0	0.0	0.0	0.0	0.0	0.0
R(%)		3.97		3.37		4.22	

Neutron diffraction experiments were carried out on the two-axis neutron diffractometer with neutrons of 1.184 Å. The step-scan covered the range of 4°–84° in 2θ with step of 0.2°. The experiment data were analyzed using Rietveld structure refinement technique[6] based on the orthorhombic model with space group Pmmm. Scattering lengths of 0.775, 0.525, 0.702, 0.7718, 0.5805×10^{-12} cm were taken for Y, Ba, Sr, Cu, and O respectively.[7] The structural parameters, including oxygen site occupancies for different oxygen sites, determined from the best fit are summarized in Table 1.

Neutron inelastic scattering measurements were performed at room temperature using the CIAE's time-of-flight (TOF) spectrometer, operated in up-scattering mode with an incident neutron energy of 18.3 meV. The GPDOS were deduced from the TOF spectra collected over the scattering angle of 0°–90° with corrections for multiphonon contributions in a self-consistent manner. The GPDOS of the three samples are shown in Fig. 1.

From Table 1, it is clear that Sr substitution induces oxygen vacancies in Cu–O chain and no oxygen vacancy on Ba–O plane. Calculation shows that the bond lengthes of Ba(Sr)–O(4) as well as Ba(Sr)–O(1) shorten with introduction of Sr. Therefore, the bond strength increases, which results in a reduction of coordination of Ba(Sr) since Ba and Sr are definitive tow-valence elements. However, our results show that oxygen atoms fully occupy the O(4) sites which is consistent with the results of band structure calculation.[3] The O(1) atoms are the next nearest neighbours to the Ba(Sr) atoms and hence, can be removed from their sites more easily compared with O(4) atoms. It is resonable to conclude that the formation of oxygen vacancies in O(1)

sites is one cause of the depression in T_c with Sr substitution.

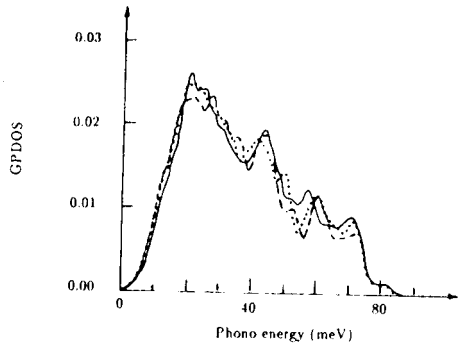

Fig. 1. GPDOS of $YBa_{2-x}Sr_xCu_3O_{7-y}$.
————$YBa_{1.5}Sr_{0.5}Cu_3O_{6.85}$
· · · · · · · · $YBa_{1.0}Sr_{1.0}Cu_3O_{6.74}$
– – – – $YBa_{0.75}Sr_{1.25}Cu_3O_{6.72}$

But oxygen vacancy can not explain the T_c depression thoroughly because the T_c of Sr substituted material is lower than that of the corresponding (with the same y) nonsubstituted material from the comparison of our results with that of Jorgensen.[8] However, our GPDOS measurements show that with increase of x the average GPDOS become softer, which implies that Sr substitution reduces the whole crystal stability. The measurements of thermal decomposition for $YBa_2Cu_3O_{7-y}$ suggest that the reduction of crystal stability would yield a depression in T_c.[9] Therefore, the reduction of crystal stability induced by the substitution of Sr for Ba may play a role in T_c depression.

In addition to the above, in Fig. 1, there is a pronounced peak shift from 57 meV for sample 1 (x=0.5) to 60 meV for sample 3 (x=1.25). In order to understand that phenomenon further, Born-von-Karman model calculation was made. Within this model the interaction with a neighbouring atom is described by one longitudinal and one transversal force constant. The force constants were obtained through adjustment to give a good fit to the experimental GPDOS. We noticed that the shift of the 57 meV peak can be realized by increasing the interaction between Cu(1) atom and O(4) atom. This suggests that the introduction of Sr strengthens the coupling between the Ba–O plane and Cu–O chain, which cripples the one dimensional characteristics of Cu–O chain and might result in T_c depression of Sr substituted material. In conclusion, our experimental results suggest that the increase of oxygen vacancies in Cu–O chain, decrease of crystal stability and the increase of the coupling between the Ba–O chain are the three possible causes comprehensively affecting the high-T_c superconductivity of Sr substituted YBa_2-Cu_3O_{7-y}.

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