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Shift of x-ray-photoelectron core levels in $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$: An explanation by bond-valence-sum calculation

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Shifts of the binding energies of x-ray-photoelectron core levels are observed in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system when x is varied. It is pointed out that this is due to the change in the chemical environment associated with the changes of the interatomic distances. We show that the so-called bond-valence-sum calculation is useful for the explanation of the shift, and propose that this method is generally applicable in explaining or predicting the shift of core levels in any system with a variable composition.

In the x-ray photoelectron spectroscopic (XPS) studies of various high-T_c superconductors and their related compounds, it is interesting that, as the composition of the system is varied—resulting in changes in the physical and superconducting properties—shifts of the core levels are observed for some systems,[1-3] but not for others.[4,5] At present, most of the XPS core-level studies of various systems are discussed separately and it seems that there is no quantitative method to explain the shift of core levels in a universal way.

Because core-level binding energies (BE) of an atom in a solid are effectively determined by its chemical environment, it is considered that change of the core-level BE reflects change of the chemical environment. Next, it is noted that the factors that determine the chemical environment of an atom are the species, the coordination number, and the configuration of its ligands. The interatomic distances between the atom and those surrounding ligands are also important. Consequently, it is natural to think that the shifts of the core levels as the system is varied result essentially from changes in these factors. The problem is how one can quantitatively evaluate the relationship between the core-level binding energy and these factors effectively, so that the relationship is applicable in a universal way.

In this context, a bond-valence-sum (BVS) method, from which the relationship between the factors determining the chemical environment and the effective local valence can be quantitatively deduced, is worth noting.[6] Since there is a general tendency for the core-level BE of an atom to become higher (lower) in an environment with higher (lower) valence, it is interesting whether the shift of core levels can be discussed in terms of the change in the effective valence deducible from this method.

In this Rapid Communication, we report on the XPS core-level results for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system. The shifts of the core levels as x is varied are observed. Bond-valence-sum calculations are performed based on the existing structural data for $Bi_2Sr_2CaCu_2O_y$ and estimated structural data for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ (with $x > 0$). The efficacy of this method for understanding the shift of the core levels in this system is discussed.

Polycrystalline $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ samples were prepared by the usual solid-state method. Appropriate mixtures of Bi_2O_3, $SrCO_3$, $CaCO_3$, Y_2O_3, and CuO were calcined at 850 °C for 10 h in air, then ground and pressed into pellets. The pellet with $x = 0$ was sintered at 848 °C, and the others with $x > 0$ at 908 °C, for 30 h in air. X-ray-diffraction patterns revealed no impurity phases. Sample preparation and characterization are described in detail elsewhere.[7] High-quality single-phase polycrystalline $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ samples with $x = 0$, 0.5, 0.8, and 1.0 obtained by this method were used in this study.

Measurements were made in an ultrahigh vacuum (UHV) system equipped with an Al x-ray source ($h\nu = 1486.6$ eV) for XPS. The resolution of the photoelectron energy analyzer was set at 0.8 eV. Core-level binding energies were referenced to the C 1*s* peak at 285.0 eV to account for the surface chargeup, especially in the case of samples that were poor electrical conductors. Each sample was scraped *in situ* under UHV conditions before measurement in a preparation chamber attached to the analysis chamber. Pressure in the analysis chamber during measurement was typically 2×10^{-10} Torr. Typical measurement time was less than 30 min, which is the approximate time the surface can be contaminated by adsorption under this pressure.

In Figs. 1(a)-1(f), XPS core-level spectra of the constituents from $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ with different x's are shown. It is obvious that as x is varied from 0 to 1, i.e., from superconducting to nonsuperconducting regions, core levels of all of the constituents move toward higher BE values. The size of the shift of each constituent is shown in Fig. 2 as a function of the yttrium composition x. The range of the shift is about 1 and 0.3 eV for Sr $3d_{5/2}$ and Bi $4f_{7/2}$, respectively. For the other core levels, the ranges of the shifts are in between the above values. Since the observed shifts of all constituents are different, it is clear that the results were not due to surface chargeup which, if it had occurred, would result in an equal (parallel) shift of all of the core levels.

While no detailed discussion was given, shifts of the core levels in this system have also been observed by Shichi *et al.*[1] Similar results can be pointed out in the report of Tanaka *et al.* for $Bi_2Sr_2Ca_{1-x}Nd_xCu_2O_y$.[2] Thus, the observed shift of the core levels seems to be intrinsic for

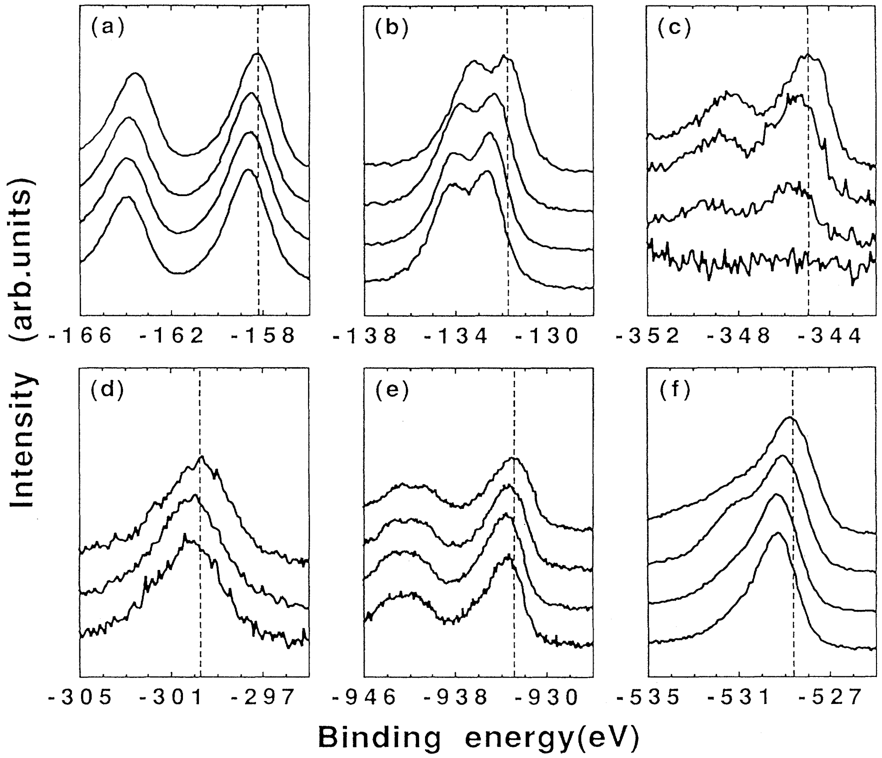

FIG. 1. XPS core spectra of (a) Bi 4*f*, (b) Sr 3*d*, (c) Ca 2*p*, (d) Y 3*p*, (e) Cu $2p_{3/2}$, and (f) O 1*s* from $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ with $x=0$, 0.5, 0.8, and 1.0 (from top to bottom). For Y 3*p*, $x=0$ is omitted.

these $Bi_2Sr_2Ca_{1-x}M_xCu_2O_y$ ($M=$Y,Nd) systems.

It is interesting to note that while the shifts of the core levels were observed in this $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system, which is metallic (superconducting) for $x<0.6$ and semiconducting for $x>0.6$, no shift of the core levels was observed in the $Ba_{1-x}M_xBiO_3$ ($M=$K,Rb) system, where superconductivity appears for *x* around 0.3–0.4, in the single-phase stoichiometry range of $0\leq x\leq 0.4$.[4] In the Zn-substituted $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_y$ system, where superconductivity disappears for $x>0.03$, it is also reported that no shift of the core levels was observed for $0<x<0.04$.[5] It appears that upon varying the stoichiometry or the composition of a system resulting in change in physical and structural properties, for some systems the XPS core levels shift, while for others they do not.

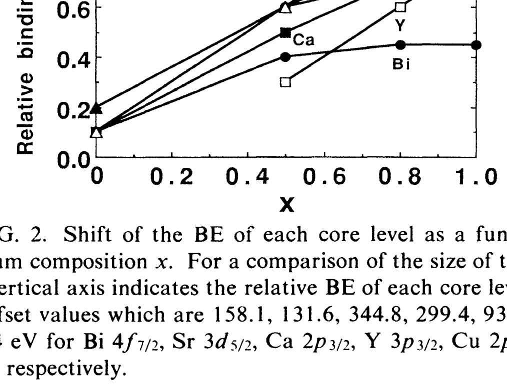

FIG. 2. Shift of the BE of each core level as a function of yttrium composition *x*. For a comparison of the size of the shift, the vertical axis indicates the relative BE of each core level from its offset values which are 158.1, 131.6, 344.8, 299.4, 932.7, and 528.4 eV for Bi $4f_{7/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, Y $3p_{3/2}$, Cu $2p_{3/2}$, and O 1*s*, respectively.

As described above, to our knowledge there exists no quantitative method to explain or discuss how the core levels of a constituent of a system will be affected upon changing the system. However, we will point out here that the bond-valence-sum method is promising. In this method, an expression, which is derived empirically from structural data of a large number of known compounds, is used to calculate the effective valence of a cation (anion) from its interatomic distances to the surrounding anions (cations).

V_i, the effective-valence or bond-valence sum (BVS) of the *i*th atom in a solid, is determined by the expression,

$$V_i=\sum_j S_{ij}=\sum_j \exp[(r_0-r_{ij})/0.37]\,,$$

where r_0 is empirically determined for each *i*-*j* atomic pair and r_{ij} is the interatomic distance between the *i*th and *j*th atom. $S_{ij}=\exp[(r_0-r_{ij})/0.37]$ can be considered to be the effective charge in the r_{ij} bond. V_i is then obtained as the sum over *j* of all of the S_{ij}'s. From the derivation of V_i, it is evident that among the factors affecting the chemical environment, the interatomic distance is left explicitly in the expression, while the species, the coordination number, and the configuration of the *i*-*j* atoms are effectively incorporated into the value of r_0. Thus V_i is in a form readily suitable for a discussion of the change in the chemical environment of a system as the composition is varied, for example, by substitution. A change in r_{ij} associated with a change in the composition will affect the corresponding S_{ij}, and thus will affect V_i if the sum over the S_{ij}'s changes.

Since V_i is a value that effectively involves all of the factors determining the chemical environment, while the core-level BE of an atom is determined by these factors, it is natural to think that one may use the bond-valence sum V_i as a parameter for a quantitative discussion of the shift of the core-level BE in a system with a variable composition.

To investigate this conjecture, the bond-valence-sum calculation for the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system was performed. Unfortunately, since no systematic neutron-diffraction structural study for this system is available, a precise bond-valence-sum calculation was not possible. However, we have estimated the structural data for this system from the neutron-diffraction data of Bordet *et al.*[8] for $Bi_2Sr_2CaCu_2O_y$ and the x-ray-diffraction data of Tamegai *et al.*[9] for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$. Based on these estimated data, bond-valence sums were calculated. The results for the $x=0$ and 1 compositions are shown in Table I. From the x-ray study, the lattice parameters of this system change continuously as x is varied.[9] With increasing x, the c axis decreases, while the a and b axes increase. When x is varied from 0 to 1, the change of the c axis is ten times larger, about 0.5 Å, compared with that of the a and b axes, where the change is about 0.05 Å. It is this large change of the c axis relative to the a and b axes that considerably changes the chemical environment of the constituents; this can be clearly seen as the considerable increase of the BVS of the Bi, Sr, Ca, and Y cation sites in Table I.

TABLE I. Interatomic distances, r_{ij}, and bond valence sums (BVS) of $Bi_2Sr_2CaCu_2O_y$ and $Bi_2Sr_2YCu_2O_y$.

	$Bi_2Sr_2CaCu_2O_y$		$Bi_2Sr_2YCu_2O_y$	
Cation site	r_{ij}(Å) [a]	BVS	r_{ij}(Å) [b]	BVS
Bi-O ($r_0=2.094$)				
Bi-O(2)	2×2.707	0.382	2×2.727	0.361
Bi-O(2)	2×2.710	0.378	2×2.730	0.359
Bi-O(2)	1×2.850	0.130	1×2.775	0.159
Bi-O(3)	1×1.890	1.736	1×1.815	2.126
		2.626		3.005
Sr-O ($r_0=2.118$)				
Sr-O(1)	4×2.550	1.245	4×2.475	1.524
Sr-O(3)	2×2.875	0.259	2×2.895	0.245
Sr-O(3)	2×2.875	0.259	2×2.895	0.245
Sr-O(2)	1×2.942	0.108	1×2.867	0.132
		1.871		2.146
Ca-O ($r_0=1.967$)				
Ca-O(1)	8×2.566	1.585	8×2.497 [c]	1.910 [c]
Y-O ($r_0=2.019$)				
Y-O(1)	8×2.516 [d]	2.088 [d]	8×2.497	2.198
Cu-O ($r_0=1.679$)				
Cu-O(1)	4×1.914	2.120	4×1.934	2.008
Cu-O(3)	1×2.645	0.074	1×2.570	0.090
		2.194		2.098

[a] From data of Bordet *et al.* (Ref. 8).

[b] Estimated based on data for $Bi_2Sr_2CaCu_2O_y$ of Bordet *et al.* (Ref. 8) and for $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ of Tamegai *et al.* (Ref. 9).

[c] Estimated value for $Bi_2Sr_2Ca_{0.2}Y_{0.8}Cu_2O_y$.

[d] Estimated value for $Bi_2Sr_2Ca_{0.5}Y_{0.5}Cu_2O_y$.

As described above, in general the core-level BE of an atom is higher in an environment with higher valence. Thus the BE of a core level should become higher for a larger BVS value. From this point, it is clear that one can use the BVS calculation to discuss the shift to higher BE of the core levels of Bi 4*f*, Sr 3*d*, Ca 2*p*, and Y 3*p* in this system. The range over which the core-level BE varies depends on the element and also on the specific core level. It can be as large as 10 eV for some core levels of some elements. On the contrary, there are cases for which the core levels are insensitive to, or show a complicated change in, various environments. The fact that the Sr 3*d*, Ca 2*p*, and Y 3*p* core levels are sensitive to changes of the chemical environment, while this is not the case for Bi 4*f*,[10] could be possible reasons for the differences in the size of shift observed. The shifts are large for Sr, Ca, and Y while small for Bi, although for the changes in BVS the opposite is true (see Fig. 2 and Table I).

For the Cu $2p_{3/2}$ levels, while the Cu $2p_{3/2}$ peaks showed a shift similar to that of the other constituents, it is pointed out from Table I that, in regard to the calculated BVS, a result in contrast with the other constituents described above was obtained: The BVS for Cu in $Bi_2Sr_2YCu_2O_y$ is smaller than that in $Bi_2Sr_2CaCu_2O_y$. By a different method of estimation, the similar tendency of the copper valence in this system has also been reported by Groen, Leeuw, and Feiner.[11] It is also noted that Cava *et al.* have reported for the $YBa_2Cu_3O_y$ system that the BVS of the in-plane Cu is smaller in nonsuperconducting compositions than that in superconducting compositions.[12]

For the Cu $2p_{3/2}$ core levels in a divalent environment, it is well known that because of the strong *p*-*d*-hole interaction, the XPS spectra consist of two final-state components, i.e., the $|2p^53d^9\rangle$ satellite peak at higher BE and the $|2p^53d^{10}\underline{L}\rangle$ main peak at lower BE, where $\underline{L}$ indicates a hole in a ligand orbital. The BE of the $|2p^53d^{10}\underline{L}\rangle$ main peak depends on both the surrounding ligands and the many-body effects involved. Generally, this results in a broadening of this peak. Thus it is not so simple to discuss how this main peak will shift as the chemical environment changes. In fact, the BE and the shape of the Cu 2*p* peaks show a complicated behavior for different compounds.[10] We conclude that in the case where the interaction with ligands is important, one has to be careful in using the BVS calculation to discuss the shift of the core levels. In such a case, other core levels of the same species, for which the interaction described above is not important, may be used instead. For example, we may use the Cu 3*s* core level to replace the Cu 2*p* core level in the BVS consideration, keeping in mind that the intensity of the former is very much lower compared with that of the latter.

For the O 1*s* core level, since there are several nonequivalent oxygen sites in a unit cell, it is difficult to relate the calculated BVS for an individual oxygen site to the shift of the O 1*s* spectrum in which the contributions of all oxygen sites are involved. Though not included in Table I, we have calculated the BVS for the oxygen sites and found that as x increases, the BVS of each site increases. The average BVS of oxygen increased from -1.87 to -2.09 for the $x=0$ and 1 samples, respectively. Thus, the shift to higher BE of the O 1*s* core level can be understood also from this calculation.

In contrast to this study it is noted that in the case of the $Ba_{1-x}M_xBiO_3$ and $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_y$ systems, where the shift of the core levels as a function of x was not observed, we have also performed the BVS calculation and concluded that although the lattice parameters change as the composition is varied, the bond-valence sums of the constituents do not change.[4,5] For these systems, changes in a particular S_{ij} associated with a change in r_{ij} are compensated by changes in other S_{ij}'s, so that the sum V_i remains unchanged.

Since the bond-valence sum gives information on local charge distribution, the implication for the occurrence of superconductivity is interesting. Already there exist some reports on this matter.[12-14] It is interesting to note that Cava *et al.* have calculated—using the precise structural parameters obtained from a neutron-diffraction study—the BVS of the $YBa_2Cu_3O_y$ system for various oxygen contents, and pointed out a close relationship between T_c and the BVS of the in-plane Cu.[12] That result seems to indicate the direct significance of the local charge, i.e., in-plane carriers, for the occurrence of superconductivity. It will be of great interest if this kind of relation can be observed in other high-T_c cuprate systems. For a systematic investigation from this point of view, precise structural data for various high-T_c systems with variable compositions and related compounds are extremely important.

In summary, shifts of the binding energies of the XPS core levels are observed in the $Bi_2Sr_2Ca_{1-x}Y_xCu_2O_y$ system when x is varied. It is pointed out that this is due to the change in the chemical environment associated with the change of the interatomic distances. We showed that one can evaluate the change in the chemical environment quantitatively by the BVS method, and the result can be used to explain why the core level shifts, and in which direction it should shift (to higher or lower BE). It is also useful in predicting how a core level will shift upon varying a system, once the structural data are known. The generality of the method makes it applicable to any system with a variable composition.

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