

X-ray Photoelectron Studies of High-temperature Superconductors: Evidence for the Importance of Alkaline Earth Metals*

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Abstract

All high-temperature superconducting ceramics so far studied contain alkaline-earth ions, and in all cases core-level X-ray photoelectron spectroscopy shows an anomalous low-binding energy peak from these ions. We argue that this may point to electron-rich alkaline earth layers. These should be highly polarisable, allowing them to facilitate superconductivity by screening the repulsion between electrons and/or holes in the CuO layers.

The application of core-level X-ray photoelectron spectroscopy (XPS) to the well characterised high- T_c (HTSC) compounds $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ (1–2–3) and $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($\text{M} = \text{Sr}, \text{Ba}$) has revealed a number of anomalous features. We focus here on significant anomalously low binding energy (low-BE) contributions to the alkaline earth envelopes. These have been observed for the Ba 3d and Sr 3d levels in our own investigations (Healy *et al.* 1988*a*, 1988*b*; Myhra *et al.* 1988). Many other groups (e.g. Steiner *et al.* 1987*a*, 1987*b*; Werfel *et al.* 1988) have also seen this effect. Furthermore, low-BE alkaline earth anomalies, similar to those in the XPS data, have also recently been observed in soft X-ray emission from HTSC compounds (Crisp, personal communication 1989). Our recent XPS studies (Bocquet *et al.* 1989*a*) of the HTSC compounds $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ have shown similar anomalies (see Figs 1 and 2), suggesting that a low-BE alkaline earth XPS signal may be a general property of HTSC compounds. A summary is shown in Table 1. By comparison the structurally similar, but non-superconducting Aurivillius phase compounds (Withers *et al.* 1988) do not exhibit low-BE signals (Bocquet *et al.* 1989*b*). Binding energies for the anomalous features are unusual, typically 2–3 eV below the values for the corresponding alkaline earth oxides, and 0.5–2.0 eV below those for the alkaline earth metals themselves.

Apparent negative binding energy shifts in core-level XPS are usually attributed either:

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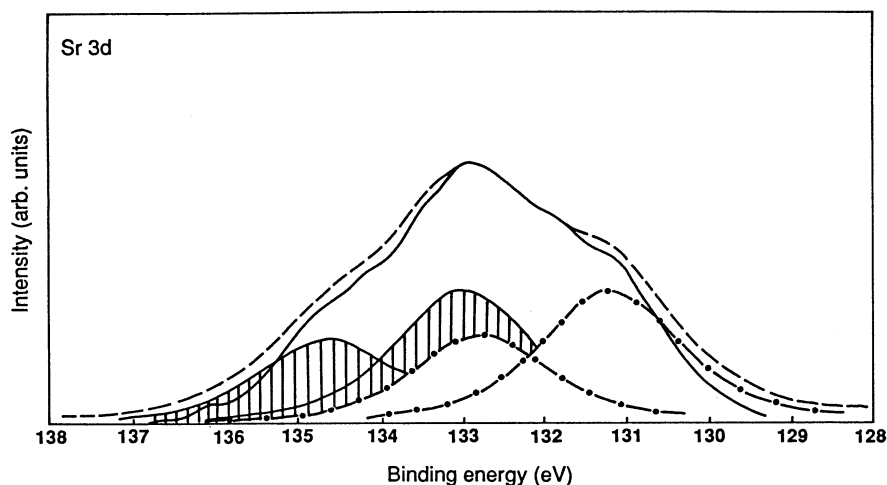


Fig. 1. Results of peak-stripping a typical Sr $3d_{5/2,3/2}$ doublet envelope of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ superconductor. The dash-dotted curves indicate the low-BE contributions, while the hatched areas define the high-BE contributions. The experimental envelope is defined by the solid curve, while the sum of the synthetic envelopes is denoted by the dashed curves. [Source: Bocquet *et al.* (1989*a*).]

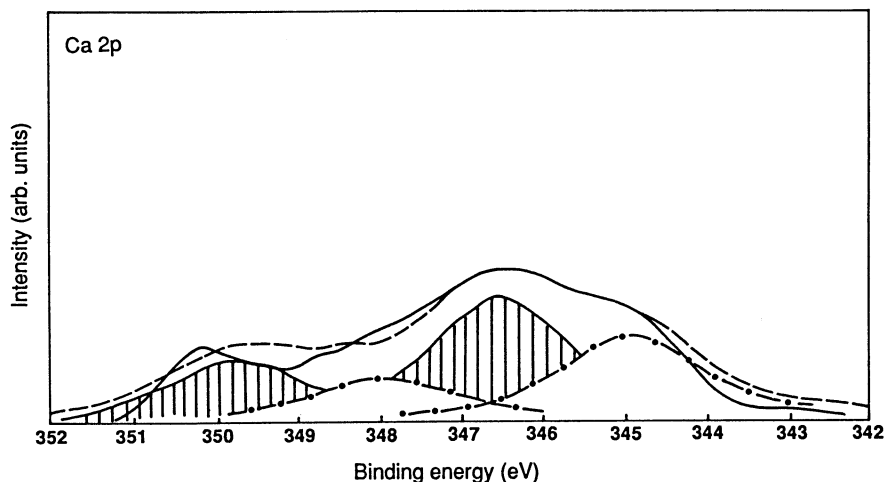


Fig. 2. $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ data as for Fig. 1, but for the Ca $2p_{3/2,1/2}$ doublet.

- (a) to additional electron density present on the species in question, compared with the reference compound, so that the departing XPS electron sees additional shielding (i.e. screening) of the ionic charge, lowering the apparent binding energy of the core state ('initial-state screening'); or
- (b) to a many-body rearrangement of electron density as a result of the sudden removal of the core electron. (When the apparent binding energy is thereby reduced, this final-state phenomenon is termed 'shakedown'.)

Table 1. Binding energies (eV) of the 'normal' and the low binding energy (LBE) lines in core-level XPS of the alkaline earths in high- T_c superconductors

Compound		Normal	LBE	Shift (LBE-normal)
Bi ₂ Sr ₂ CaCu ₂ O ₈ ^A	Sr 3d _{5/2}	133.8	132.2	-1.6
	Ca 2p _{3/2}	346.6	344.8	-1.8
Bi ₂ Sr ₂ CuO ₆ ^A	Sr 3d _{5/2}	133.5	131.7	-1.8
YBa ₂ Cu ₃ O _{7-x} ^{B,C}	Ba 3d _{5/2}	779.6	777.8	-1.8
HoBa ₂ Cu ₃ O _{7-x} ^C	Ba 3d _{5/2}	779.9	778.0	-1.9
La _{2-x} Sr _x CuO ₄ ^D	Sr 3d _{5/2}	138.8	132.5	-1.3

^A Bocquet *et al.* (1989a). ^B Healy *et al.* (1988b).^C Healy *et al.* (1988a). ^D Steiner *et al.* (1987a).

We have no compelling experimental evidence to distinguish between mechanisms (a) and (b) above. We note, however, that the lineshapes of the low-BE peaks tend to resemble those of the alkaline earth peaks in reference alkaline earth oxides. This tends to favour mechanism (a) above, since in a one-electron picture, initial-state screening tends simply to shift the relevant line along the energy axis, unlike shakedown which is expected to lead to lineshape modifications.

From recent discussions (Maslen, personal communication 1989) we understand that there is high-resolution X-ray diffraction data on the 1-2-3 compounds suggesting an anomalously large integrated electron density near the Ba cores. This also tends to support mechanism (a) above.

An initial-state explanation runs into difficulties, however, when one considers the bulk of electronic band structures calculations for the HTSC compounds, as these mostly show the alkaline earths in a relatively normal divalent condition. For example, Mattheiss (1987), Yu *et al.* (1987a, 1987b), Massida *et al.* (1987), Freeman *et al.* (1987) and Szpunar and Smith (1988) have all predicted normal divalent Ba in the 1-2-3 compounds. Similarly, Hybertson and Mattheiss (1988) and Krakauer and Pickett (1988) have predicted simple divalent Sr and Ca cations for the Bi-based HTSC compounds. Caution is required when applying these calculations to the present debate, however, as there is, to date, no satisfactory basic theory of the band structure of highly correlated electronic systems such as these. Furthermore, there are a few calculations (Fletcher 1988; Timoshevskii 1987) suggesting the presence of f-bands near the Fermi energy which might allow for abnormal properties. Thus, the bandstructure literature need not necessarily be taken as invalidating any initial-state model.

If an initial-state screening mechanism were indeed to prove responsible for the low-BE alkaline earth XPS features, some interesting consequences might follow. For example, one might speculate that the alkaline earth layers are metallic, or that the conducting paths of charge carriers include both the CuO layers and the alkaline earths on adjacent layers.

A less radical proposal is that the alkaline earth layers are merely richer in relatively weakly bound electrons than assumed in the standard view. Then they could serve as 'screening layers', highly polarisable because of the unfilled shells on the alkaline earths (whose atomic forms are known to be exceptionally polarisable). Such a screening layer could weaken the Coulomb repulsion between charge carriers located in the nearby CuO layers. (A simple

classical analogy involves two point charges near a grounded perfect-metal surface, the latter representing an extreme case of an adjacent screening layer. Here each charge appears attracted to the other's image charge, leading to a weakening of their mutual Coulomb repulsion). In conventional models of superconductivity, such a weakening would raise T_c by helping charge carrier pairs to bind.

In a recent paper, Ronay and Newns (1989) have also suggested that the polarisability of alkaline earths is significant in promoting the high- T_c superconductivity of certain compounds. Their evidence comes from the higher T_c of barium-containing compounds, compared with that of analogues in which Ba is replaced by the less polarisable Sr. They also showed that such polarisability in nearby layers can affect the T_c of CuO layers even in a nonconventional model of superconductivity, where the effect occurs through reduction of the on-site repulsion parameter U in the Hubbard model.

We feel that our observations, combined with those of Ronay and Newns (1989), Maslen (personal communication, 1989) and Crisp (personal communication, 1989) do indeed add up to a significant case for an important (and, we feel, ubiquitous) electronic role for the alkaline earth species in high-temperature superconductivity.

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