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Soft X-ray Absorption and Emission Spectra and the Electronic Structure of some Exotic Materials

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ABSTRACT

The technique of soft x-ray fluorescence spectroscopy (SXE) is complimentary to that of photoemission spectroscopy (PES). SXE probes the local partial density of states (PDOS), selects dipole allowed symmetries, and is not necessarily surface sensitive. PES on the other hand, averages over the DOS and can be used to measure the dispersion of the energy bands. PES is also very surface sensitive. We present measurements on the high T_c superconductors, the quasicrystalline phase of AlMn, and the LiAl intermetallic alloy. These measurements provide insight for theoretical modeling. In the case of the high Tc compound and the intermetallic compound the measurements are in good agreement with the theory. However, for the quasicrystals the measurements provide new insights to challenge theory.

1: INTRODUCTION

Soft x-ray emission (SXE) spectra produced by dipole transitions from valence states characteristic of the solid to core states of a particular atom in the solid provides important information about the electronic states of solids. X-ray emission spectroscopy differs significantly from other techniques to investigate the electronic structure of solids. For example photoelectron spectroscopy (PES) is an important tool used to study the band structure of solids, but it is very surface sensitive, and when used as a band structure probe, is not atomic site specific and probes bands of all symmetries. SXE on the other hand is not necessarily surface sensitive, projects out bands of a specific symmetry allowed by dipole selection rules and is sensitive to the partial density of states (PDOS) at particular atomic sites. Thus, SXE provides complementary information to that obtained from PES.

SXE provides information about PDOS selected for its angular momentum symmetry properties. This feature makes SXE especially valuable for the study of the electronic structure of multi-element solids such as alloys and other compounds where the local and chemically selective nature of the probe have particular value. In this paper we present a few examples where the special advantages of SXE spectroscopy have been exploited.

In spite of these advantages SXE spectroscopy has not flourished in the same way that PES and X-photoelectron spectroscopy have. The major drawbacks that have limited the usefulness of SXE spectroscopy have been the low fluorescence yield of low Z materials and the difficulty of working in the soft x-ray spectral region, where extreme grazing incidence is required on optical surfaces for adequate reflectivity in the soft x-ray spectral region.

The work we will report on has been carried out on a very high sensitivity instrument that has been developed[1] in our group and installed at the National Synchrotron Light Source at Brookhaven National Laboratory. Through the use of this instrument, which has a sensitivity about 10^3-10^4 times greater than spectrometers of a more conventional design , we have been able to undertake a number of studies on materials such as dilute aluminum impurities in a magnesium host matrix, and the technologically important $Al_xGa_{1-x}As$, where x was varied from 0.05 to 0.80.

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DISCLAIMER

2: HIGH T_c SUPERCONDUCTORS

In this section we present measurements of soft x-ray emission and total photoelectron yield of $Ba_2YCu_3O_{7-x}$. The samples were prepared at NBS by sintering and heat treating copper and yttrium oxide and barium carbonate in an oxygen atmosphere according to proven recipes. The superconducting nature of the samples was verified by a.c. magnetic susceptibility measurements, and T_c was found to be 90K. The transition temperature zone had a width of few degrees. Our total photoelectron yield measurements near the 3p ionization threshold in Cu (Fig. 1a) support the contention that Cu is in the +2 valence state.[2-5] We have used electron-beam excited soft x-ray emission spectra to measure the p-type partial density of states (p-PDOS) localized on O, Ba, and Y sites. For the elements (Y, and Ba) the major peak in the soft x-ray emission spectra lies between 3.0 and 4.0 eV below e_F (Fig 1b). These two elements are not major contributors to the DOS, but do show overlap with the DOS observed localized at the O sites by O K emission at a photon energy of about 525 eV. The maximum in the DOS occurs about 2.3 eV below threshold. The energy corresponding to the transition between the Fermi edge and the core hole was determined with the aid of the absorption spectrum[6]. We have also observed the L_{23} emission spectrum of Cu in $Ba_2YCu_3O_{7-x}$, which maps out valence states of d symmetry. The maximum in the PDOS in this case lies about 2.5 eV below e_F. These observations place the d and p bands at about the same energy. Thus the bands will be strongly hybridized. The shape and energy position are in surprisingly good agreement with a calculations[3] of the emission using a one electron model. The present measurements have been made both at room temperature and at 85K. No difference in the p-PDOS was observed at the two temperatures. This is consistent with observations that $Ba_2YCu_3O_{7-x}$ does not undergo a structural phase change between T_C and room temperature.

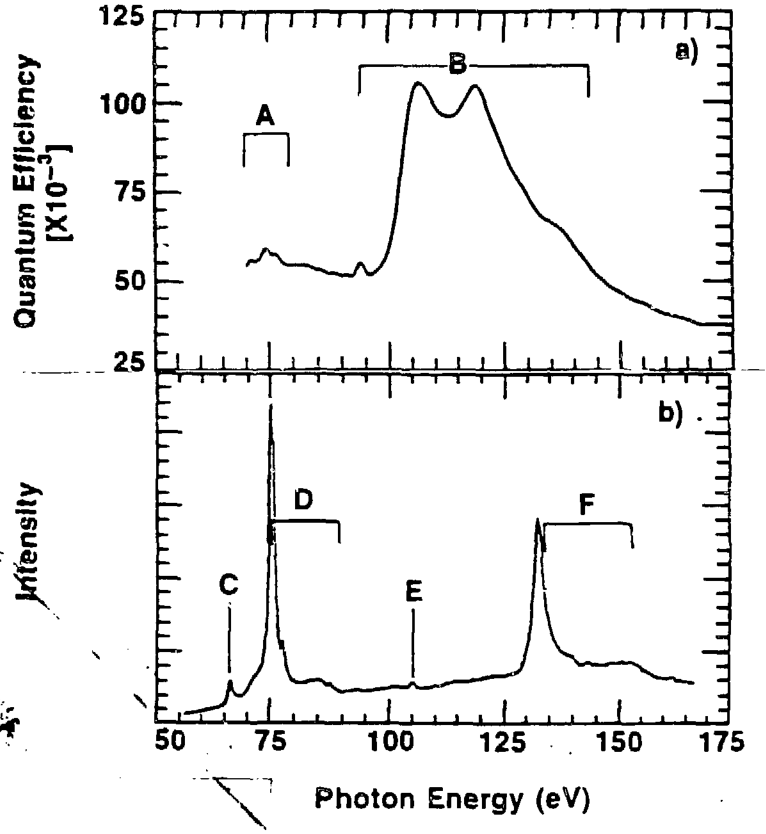

Figure1:

a) Total quantum yield for superconducting $Ba_2YCu_3O_{7-x}$ as a function of the photon energy. A defines the energy region corresponding to that required for the promotion of a 3p core electron in Cu to the conduction band. The energy band denoted by B is the absorption by 4d core electrons in Ba.

b) Intensity of soft x-ray fluorescence excited by 2 keV electrons vs. photon energy. C denotes the energy position of the $N_{2,3}M_{4,5}$ transition in Y in second order reflection from the grating; F is the first order signal of this transition. The peak E is the O K emission band appearing 5th order diffraction. D is the energy region corresponding to Ba inner shell transitions $O_{2,3}N_{4,5}$ and transitions between the valence electrons and the Ba 4d hole states.

3: QUASICRYSTALINE PHASES OF AL-MN ALLOYS

As a second example we look at the emission from aluminum in aluminum-manganese alloys. Intermetallic phases have been discovered[7] which exhibit icosahedral or decagonal (T-phase) symmetries that are impossible for ordinary crystalline material. There have been many interpretations of the structure of this material. One would like to determine where the atoms are with respect to sites in the unit cell, the tiles, or the structural element. This important quantity has not been definitively established. Furthermore the nonperiodic structure of these materials makes the calculation of the band structure a challenge. Several authors[8-10] have modeled the electronic properties of these materials, but there has been almost no measurement of their band structure. Soft x-ray emission (SXE) yields valence band emission spectra proportional to the partial density of states (PDOS) localized at the emitting atom. We report the first measurement of the SXE spectra of the $L_{2,3}$ emission bands in the icosahedral and decagonal (T phase) and the related alpha cubic phase of Al-Mn-Si

The measurements were made using a melt spun ribbon prepared at the NBS. Our ultra sensitive soft x-ray spectrometer[1] was used to obtain the spectra, which were excited by an electron beam. The results are summarized in Figure 2. Fig. 2a) is an enlargement of the spectral range near the photon energy corresponding to transitions of the electrons near the Fermi energy ε_F to 2p core holes. Fig. 2b) shows a comparison of the PDOS between 62 and 67 eV, corresponding to small values of the k vector.

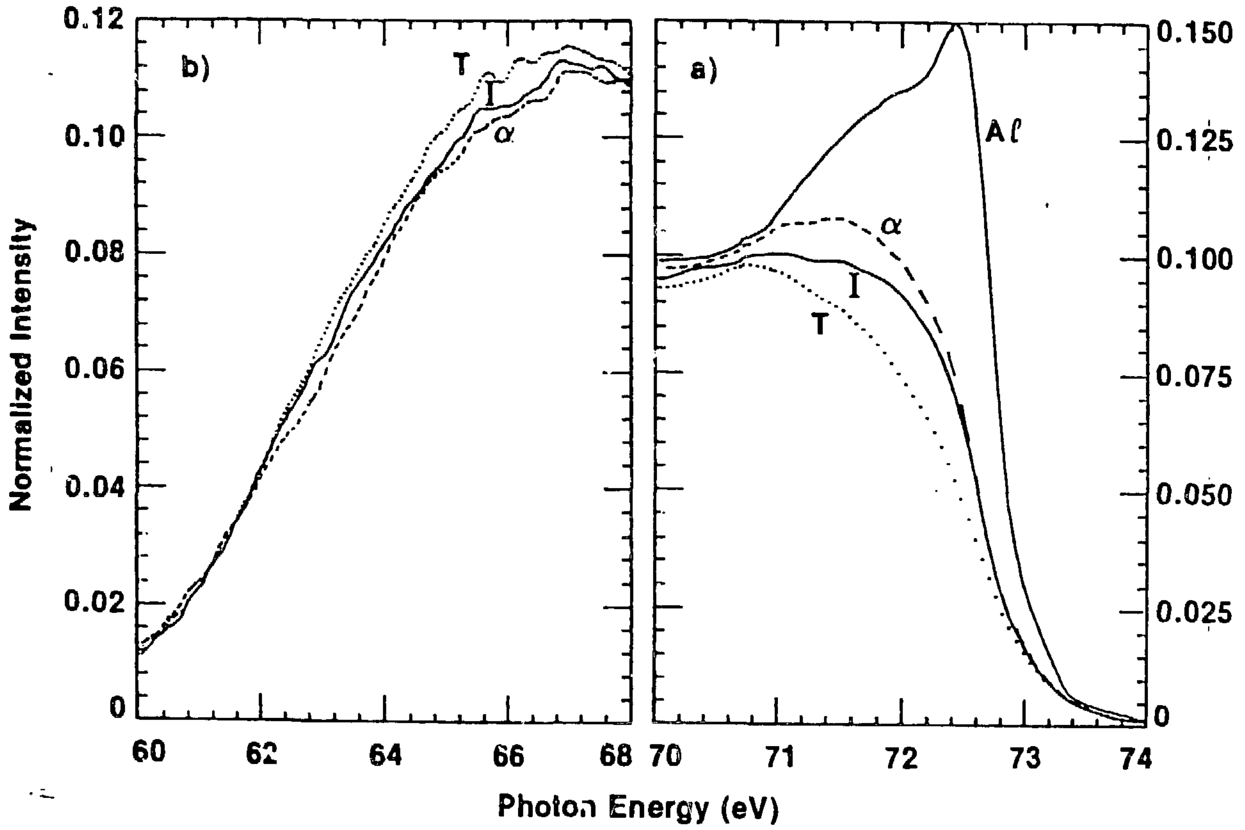

Figure 2:

a) The SXE spectra of AlMn alloys on an expanded scale near ε_F. Al, T, α, and I identify the curves for pure aluminum, the T phase, the α cubic phase and the icosahedral phase of the materials, respectively.

b) Shows the spectra on an expanded scale for lower photon energies.

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Summarizing these results, we find that the spectra of different alloy phases are very similar. This observation suggests that the quasicrystalline phase produces a small perturbation of the electronic density of states. We observe a chemical shift of 0.2 eV between the alloys and pure aluminum, which is consistent with the shift one would observe by accounting for the redistribution of the electrons localized at the aluminum and the change in the volume available to the electrons at the aluminum sites. We observe a chemical shift of less than 0.1 eV between alloys of the crystalline phase and the quasicrystalline phase , which contradicts one model[6] that predicted a 0.9 eV shift. We also observe a diminution in the partial DOS near e_F of the quasicrystalline alloy compared to the crystalline alloy. Two theoretical models[8,9] predict an enhancement of the DOS near e_F which was not observed. These results provide new information to guide the calculations of the electronic band structure of these materials.

4: INTERMETALLIC COMPOUNDS: LI AL

The intermetallic compound Li Al has potential value as a battery alloy, and is interesting theoretically because is is an intermetallic compound with very unusual tetragonal bonding. In the B32 crystal structure of the compound the Li and Al atoms occupy interpenetrating diamond type sublattices. [11,12] Locally the structure can be viewed as a body centered cube , in which the Al atoms have a degree of covalent bonding with nearest neighbor Al atoms and form a rigid frame for the system. The Li atoms have weak metallic bonding with both Al nearest neighbors and are very mobile; hence its value as an ionic conductor. The unusual structure of LiAl has been a challenge to theorists and there are several band structure calculations available for this compound. Two of these provide calculations of the angular momentum resolved PDOS for the two elements of LiAl [11,12].

SXE spectra of transitions between the valence band and the 1s core level of lithium produce a measure of the PDOS of p symmetry localized at the lithium sites. The aluminum spectrum, in which a 2p core hole is being filled, provides information about the PDOS of s and d symmetry localized at the aluminum site. Soft x-ray absorption spectra provide information about the density of empty states in the conduction band. The emission spectrum was obtained using our high sensitivity SXE spectrometer. The samples were prepared at Argonne National Laboratory and had a composition of $Li_{0.51}Al_{0.49}$. In the SXE measurements fresh samples were exposed by fracturing the sample in air or an inert gas immediately before mounting them in the spectrometer.

Because the material is very unstable, great care was necessary to insure the observations were indicative of the material's composition. For example, if too intense an electron beam was used to excite the sample the composition was changed and the spectrum observed was that of another phase. The results obtained near the K edge of lithium are shown in Fig. 3a. The theoretical results from the band structure calculations described in ref. 12 are shown as the dashed curve. Similar results for the aluminum L_3 SXE spectrum are shown in Fig. 3b.

There is excellent agreement between the measured SXE spectrum of Li and the major peaks in the calculated p-PDOS. All major peaks show good correlation between calculation and measurement. We note in particular that there is a large density of p states extending to about 3.5 eV below the Fermi level (corresponding to a photon energy of 52.0 eV), which does not agree with results obtained by PES.[13]

Similarly there is good accord between the calculated PDOS of aluminum and our measurements. However there is an anomaly in the measured spectrum at -6.0 eV. This peak was always present, but its intensity was found to be variable from sample to sample.

A major unresolved question about the LiAl intermetallic compound is the striking differences between the electronic densities of states determined by PES and by SXE. We suggest these differences can be understood in terms of the very different sampling depths of the two techniques. Electron spectroscopies sample at most depths of a few atomic layers, while SXE samples to depths of many hundreds of Angstroms. In this compound we have seen that the very high mobility of Li can have dramatic effects on the measured spectra. It seems likely that in a surface region, extending perhaps to several atomic layers, there is a different atomic arrangement that yields the spectra observed by PES.

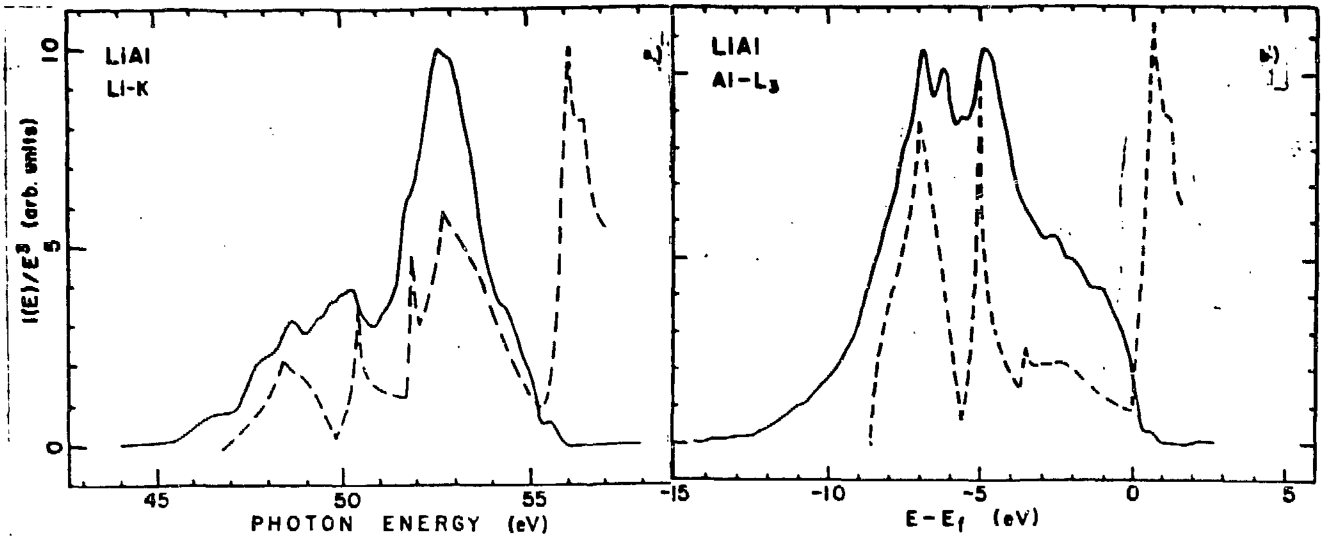

Figure 3:

a) The SXE spectrum of LiAl compared with the calculated p-PDOS of ref. 12. The spectrum is corrected for a surface layer of lithium. The energy corresponding to a transition between e_F and the 1s hole is 55.5 eV.

b) The SXE L_3 spectrum of Al in LiAl compared with the calculated (s+d)-PDOS of ref. 2. The spectrum is obtained by deconvolution from the L_{23} spectra. The Fermi level e_F is taken at 72.4±0.1 eV.

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