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Electronic structure of α-Al_2O_3 studied by polarized x-ray-emission spectroscopy

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The polarized K-emission band of Al in α-Al_2O_3 is presented. The double-peaked structure of this band shows a strong anisotropy. It is observed that when the polarization vector **e** of the radiation is parallel to the trigonal c axis of the corundum crystal, the Al $K\beta$ spectrum differs considerably from that spectrum in which **e** is perpendicular to **c**. It should be mentioned that the intensity ratio of the two-peak structure is also changed according to a "cluster" calculation although there are some discrepancies between theory and experiment which are briefly discussed.

Due to more extensive applications of corundum (α-Al_2O_3) as a structural, electronic, and optical material there is an increasing need to understand its electronic properties. Since the end of the 1960s both experimental and theoretical investigations have been made in order to study the valence- and conduction-band properties of α-Al_2O_3 (cf. Refs. 1 and 2). In the experimental investigations methods such as x-ray-emission (XES), x-ray-absorption (XAS), and x-ray-photoemission spectroscopy (XPS) were used, whereas theoretical research concentrated on band-structure as well as cluster calculations.

Among the more recently obtained theoretical results are those of an *ab initio* band-structure calculation by Causà *et al.*[2] and those of a multiple-scattering $X\alpha$ (MS-$X\alpha$) cluster calculation by Nagel.[1] Both results give the local partial symmetry of the valence-band states and therefore can be well verified by means of suitable x-ray-emission spectra.

The aim of this paper is to perform such a verification of Al $K\beta$ and O $K\alpha$ valence-band emission of α-Al_2O_3 measured for the two principal polarizations of the x-ray radiation emitted by a single-crystal sample[3] having a rhombohedral (corundum) structure.

The Al $K\beta$ and O $K\alpha$ valence-band spectra were measured with the ammonium dihydrogen phosphate (ADP) and rubidium acid phthalate (RAP) analyzing crystal, respectively, of an electron microprobe analyzer ARL EMX-SM on a corundum single crystal with an emitting surface cut parallel to the trigonal c axis and covered by a thin vapor-deposited carbon film to obtain electrical conductivity of the sample.

As described in Ref. 4 for similar measurements at TiO_2 (rutile), the spectra have been registered for two different positions of the emitting sample relative to the reflection plane of the spectrometer crystals. From the two spectra the intensities $I_{\parallel}(E)$ and $I_{\perp}(E)$ can be calculated.[3] These intensities represent the spectra with the polarization vector **e** of the emitted radiation parallel and perpendicular, respectively, to the trigonal c axis of the single crystal α-Al_2O_3.

In Figs. 1 and 2 the polarized O $K\alpha$ and Al $K\beta$ emission spectra are shown and arranged on the same energy scale. Their relative position on this scale was determined with an uncertainty of ±0.2 eV using the XPS O 1s and Al 2p core-level energies[5,6] and the Al $K\beta$ photon energy[7] of α-Al_2O_3.

The experimental spectra were compared with the O 2p and the Al 3p density of states (DOS) from the band-structure calculation of Causà *et al.*[2] in Figs. 1(a) and 2(b), respectively. These local partial DOS were aligned with the measured spectra so that the peaks A of the O 2p DOS and the O $K\alpha$ coincide on the energy scale.

Some of the results of the MS-$X\alpha$ cluster calculation for α-Al_2O_3 are given in Table 2 of Ref. 2. The ground-state energy parameters and the percentage Al 3p orbital character are subdivided into p_z orbitals (a_1 and a_2 symmetry) and $p_{x,y}$ orbitals (e symmetry). Considering that the $p_z \rightarrow s$ and $p_{x,y} \rightarrow s$ transitions produce $I_{\parallel}(E)$ and $I_{\perp}(E)$, respectively, the parameters of the cluster orbitals with a_1, a_2, and e symmetry, respectively, were used to calculate quantities resembling the local, partial (l,m)-resolved density of states (3) in the followed named "cluster" DOS. This was done by broadening the discrete cluster levels by Lorentzians having all the full width at half maximum (FWHM) equal to 0.8 eV and the peak height proportional to the percentage of Al 3p orbital character. The calculated Al 3p_z and Al 3$p_{x,y}$ cluster DOS in Fig. 2(c) was arranged with respect to the polarized Al $K\beta$ emission [Fig. 2(a)] in such a way that peak B of the p_z-like "cluster" DOS and peak B of the Al $K\beta$ emission for $\mathbf{e}\parallel\mathbf{c}$ polarization coincide in energy.

The O $K\alpha$ emission of α-Al_2O_3 shows no polarization dependence, i.e., for both polarizations $\mathbf{e}\parallel\mathbf{c}$ and $\mathbf{e}\perp\mathbf{c}$ the same $I(E)$ was measured within the limits of error. Therefore, in Fig. 1(b) only one experimental spectrum is given which depends on the relative energy E. The high-energy tail of O $K\alpha$ is extrapolated by a dashed line according to the measurement which has been made with a grating spectrometer.[8] The increase of $I(E)$ on the high-energy side of the spectrum [Fig. 1(b)] results from the

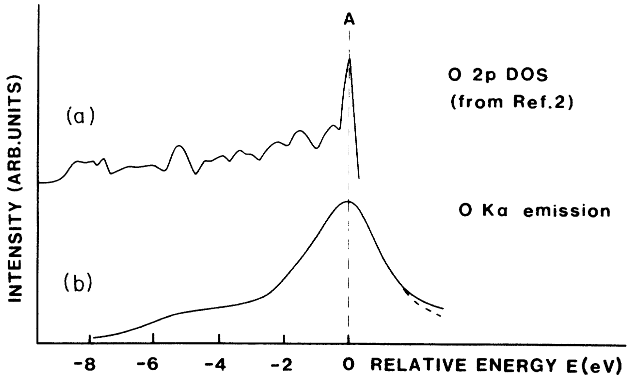

FIG. 1. (a) shows the oxygen $2p$ density of states calculated by Causà *et al.* The relative energy of the main peak A of this band structure result is chosen to be equal to zero. (b) describes the unpolarized experimental O $K\alpha$ x-ray-emission spectrum. It should be noted that the chain line is taken from Ref. 8.

anomalous peak which is appearing if the RAP crystal is used as a monochromator.[9,10]

After setting the main peak A of O $K\alpha$ [Fig. 1(b)] and that of the O $2p$ DOS [Fig. 1(a)] at the same relative energy ($E=0$), a good qualitative agreement between theory and experiment is found. Hereby, this main peak A reflecting nonbonding and/or antibonding O $2p$ states is followed by a broad band of bonding states on the low-energy side. This bonding O $2p$ band, however, is calculated to be about 3 eV broader than the estimations from the measured O $K\alpha$ would indicate.

The same seems to be true for the Al $3p$-like subband if the Al $K\beta$ emission [Fig. 2(a)] is compared with the Al $3p$ DOS in Fig. 2(b). These spectra and DOS show similar characteristic features and relative positions, i.e., nearly pure O $2p$ states on the top of the valence band (at structure A) and a strong mixing of O $2p$ with the Al $3p$ states towards the bottom of the band. The bottom of this predominant O $2p$-like valence band appears to be shifted to lower energies in the calculation of Causà *et al.*[2] causing the above-mentioned broadening of the whole upper valence band. This tendency of shifting to lower energies seems to be continued in the lower valence band of the O $2s$ states. The position of this band can be determined indirectly by measuring the Al $K\beta'$ subband where Al $3p$ states are admixed to the O $2s$ states. According to the measurements of Läuger[7] and also Dodd and Glen,[11] the center of the Al $K\beta'$ would appear in Fig. 2(a) at about -17.7 eV. On the other hand, in Fig. 1(a) the O $2p$ subband should lie at about -23.5 eV according to the band calculation of Causà *et al.*[2]

A comparison of Figs. 2(a) and 2(c) in which the peak structure B possesses the same relative energy E shows also qualitative agreement between theory and experiment. The polarization dependence of the Al $K\beta$ emission is satisfactorily reproduced by the Al $3p$ "cluster" DOS calculated from the cluster data. This means that the cluster model used in Ref. 1 is able to predict the strong anisotropy of the polarized Al $K\beta$ emission. A remarkable difference exists, however, between theory and experiment concerning the peak heights of C with respect to B. Structure C in the Al $3p$ cluster DOS [Fig. 2(c)] seems to be too small to produce the peak intensity at C in the Al $K\beta$ emission [Fig. 2(a)]. A possible reason for this discrepancy may be an energy dependence of the transition probability which also determines the emission intensity in addition to the DOS. In this connection it can be referred to calculations of the transition probabilities of the x-ray-emission spectra of FeAl.[12] There has been found a small increase of the radial transition probability for Al $K\beta$ towards the top of the valence band (Fig. 1 in Ref. 12). Such an effect reduces the discrepancy observed in the C structure of our spectra.

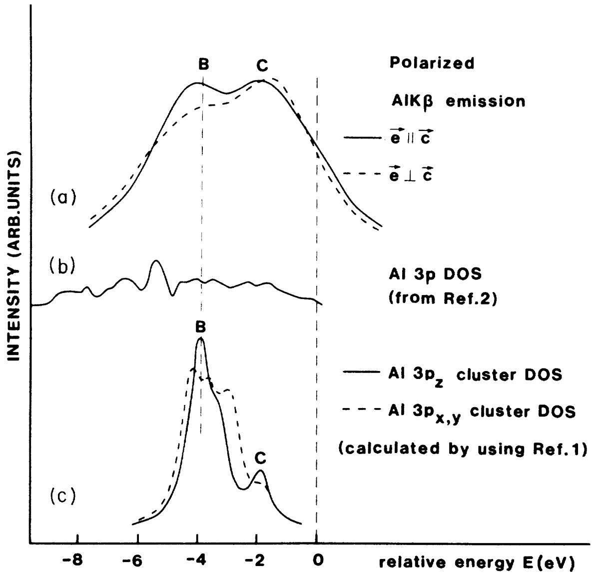

FIG. 2. (a) presents the polarized Al $K\beta$ emission bands of α-Al_2O_3 which is on the same energy scale as the spectrum in Fig. 1. The solid line describes the case when $\mathbf{e}\parallel\mathbf{c}$ and the chain line is the situation when $\mathbf{e}\perp\mathbf{c}$. (b) shows the "unpolarized" Al $3p$ DOS by Causà *et al.* (c) is the polarized "cluster" densities of states in which the solid line is for $\mathbf{e}\parallel\mathbf{c}$ and the dashed line shows $\mathbf{e}\perp\mathbf{c}$. The shape of the two-peak structure is also changed according to the "cluster" calculation.

With respect to the arrangement of the Al $K\beta$ emission and of the Al $3p$ cluster DOS in Figs. 2(a) and 2(c), respectively, further cluster states with partial Al $3p$ orbital character lie at -17.4 eV. The corresponding Al $K\beta$ emission was measured[7,11] as mentioned above at -17.7 eV on the common energy scale of Fig. 1. This indicates a good agreement between experiment and results from the cluster calculation by Nagel.[1]

On the other hand, the shape of the O $K\alpha$ emission cannot be approximated by the cluster data. The cluster DOS constructed from the O $2p$ orbital character reproduces the typical structures of the Al $3p$ cluster DOS but with different weight in comparison with this DOS. In general, however, there is no similarity with the O $K\alpha$ emission. As the model cluster used for the calculation consists of two inner Al atoms and nine outer O atoms, it is obviously inadequate to reproduce the crystal potential and wave functions of the outer atoms. This is a common problem appearing in cluster calculations for the outer atoms of great molecules or of sandwich layers in crystals, as for example in Ref. 13. Such problems can successfully be investigated by means of the conventional and/or polarized valence-band spectroscopy[3] because it provides detailed information on the participation of the valence orbitals in the different bonds and on the energy of the corresponding valence states.

In conclusion, an anisotropy is found in the K-emission band of Al in Al_2O_3 by using polarized XES. This is also suggested by a "cluster" calculation. In the case of the O $K\alpha$ emission of Al_2O_3 no polarization dependence was observed.

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