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Multiple-scattering approach to the x-ray-absorption spectra of perovskite-type compounds

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The metal *K* x-ray-absorption near-edge structure has been calculated for the first time from a multiple-scattering formalism for the perovskite-type compounds $KMnF_3$, $KFeF_3$, $KCoF_3$, $KNiF_3$, and $KZnF_3$. The calculation includes the effects of a core hole and of Madelung corrections for crystal potentials. It is shown that the results including the lifetime-broadening effect are in good agreement with the experiment of Shulman *et al.*

I. INTRODUCTION

In 1976, Shulman *et al.* investigated a series of perovskite cubic fluorides KMF_3 (M =Mn, Fe, Co, Ni, and Zn) by means of x-ray-absorption spectroscopy.[1] They measured metal *K* x-ray-absorption spectra from these compounds and observed the spectra consisting of many peaks. These spectra were interpreted by them in terms of atomic levels in the energy region within 40 eV of the absorption threshold. The purpose of the present investigation is to calculate whole spectra of the metal *K* x-ray-absorption near-edge structure (XANES) for those perovskite cubic fluorides within a multiple-scattering (MS) formalism[2] which assumes muffin-tin potentials. Mattheiss has already calculated the energy bands of several cubic perovskite-type compounds, $KNiF_3$, $SrTiO_3$, $KMoO_3$, and $KTaO_3$, using a nonrelativistic augmented-plane-wave (APW) method.[3] As far as we know, however, no report of theoretical calculations of XANES spectra has been made for the three-component perovskite cubic fluorides.

II. CALCULATION

The calculations are based on the following three parts. The first part consists of self-consistent-field (SCF) calculations[4–6] for ionized and x-ray-absorbing metal (M) atoms. The electron configurations of these atoms are $K^+(1s^2 2s^2 2p^6 3s^2 3p^6)$, $F^-(1s^2 2s^2 2p^6)$, and $M^{2+}(1s^2 2s^2 2p^6 3s^2 3p^6 3d^n)$ for the ionized atoms, and $M^{2+}(1s^1 2s^2 2p^6 3s^2 3p^6 3d^n 4p^1)$ for the x-ray-absorbing metal atoms which are subject to the *K* excitation of x-ray. Here, n denotes the electron occupation number of the 3*d* orbital and is 5, 6, 7, 8, and 10 for Mn, Fe, Co, Ni, and Zn, respectively. The SCF calculations are carried out following a prescription of Herman and Skillman[7] and using Schwarz's exchange parameter[8] for the exchange correction. The second part is the construction of crystal potentials by use of the atomic charge densities obtained in the first part. We included the Madelung correction due to charge transfer. In two-component crystals like NaCl-type ones, this correction is systematically taken into account by use of a reduced Madelung constant proposed by Johnson and Templeton.[9] In three-component crystals, however, it is necessary to evaluate it by a direct method. We evaluated the Madelung correction by Evjen's method,[10] and constructed the crystal potentials for the perovskite-type compounds KMF_3 within the muffin-tin (MT) approximation by using the same procedure as in our previous work for two-component crystals.[6] The last part is to perform final calculations for XANES using the formulation of MS which was described in Ref. 2.

In the following, we describe how the MT radius R and the MT zero V_0 characterizing the MT potentials were determined. In two-component crystals, the position and the energy of the point where the Madelung-corrected potentials $V^c(r)$ cross can be used for R and the first determination of V_0.[11,12] In our previous paper we calculated the Cl *K* XANES spectra for KCl, $SrCl_2$, and CsCl using MT parameters determined in this way and found that overall profiles of the experimental spectra for these crystals are well reproduced.[6] For three-component crystals, however, the MT parameters cannot be uniquely determined by this method, since there are two potential-crossing points for each ion. The primitive cell for the ideal perovskite structure ABC_3 contains a B atom at the body center, C atoms at each of the face centers, and A atoms at the corners of the simple cubic unit cell. We have chosen the MT radii for the metal (R_M) and fluorine (R_F) ions in such a way that the Madelung-corrected potential energies for the metal and fluorine ions cross at these MT radii in the $\langle 100 \rangle$ directions. Namely, the MT spheres for the metal and fluorine ions touch along these directions. The MT radius R_K for potassium ions was fixed to $0.4a_0$, where a_0 is the lattice constant. The use of this value for R_K minimizes non-

TABLE I. Lattice constant a_0 (Ref. 13), muffin-tin radii R_K, R_M, and R_F in atomic units, and muffin-tin zero V_0 (in eV) for KMF$_3$ (M =Mn, Fe, Co, Ni, and Zn).

Crystal	a_0	R_K	R_M	R_F	$-V_0$
KMnF$_3$	7.918	3.167	2.300	1.659	7.190
KFeF$_3$	7.790	3.116	2.254	1.641	7.561
KCoF$_3$	7.690	3.076	2.217	1.628	7.846
KNiF$_3$	7.582	3.033	2.177	1.614	8.173
KZnF$_3$	7.663	3.065	2.190	1.642	7.908

spherical corrections to the potential within the potassium MT sphere.[3] We adopted the $V_K^c(R_K)$ as the MT zero V_0, because $V_K^c(R_K)$ is greater than $V_M^c(R_M)$ and $V_F^c(R_F)$ for all the compounds. The values used for the MT radii R and MT zero V_0 are listed in Table I together with the lattice constant a_0.[13]

Finally we mention the maximum angular momentum ($l_{\max}$) and cluster size ($S_{\max}$) taken into account in the MS calculations. The $l_{\max}$ was taken as 2, and $S_{\max}$ was set to the fourth shell for final results. We have checked that a sufficient convergence was obtained with $(l_{\max}, S_{\max})=(2,4)$. The cluster is made of 45 atoms and the size of the supermatrix defined in Eq. (3a) in Ref. 2 is 405. The results of the multiple-scattering calculations were broadened to account for the lifetime of the core hole.[2]

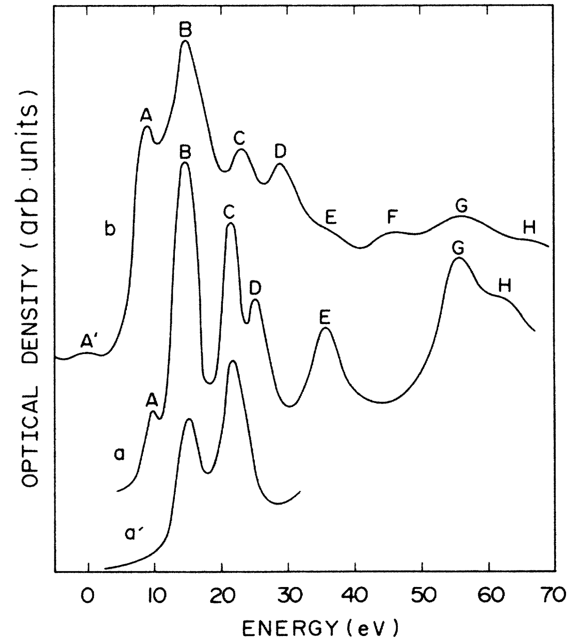

FIG. 1. Comparison of the calculated metal K XANES spectrum with the experimental one for KMnF$_3$ taken from Ref. 1. Curve a denotes the calculation and curve b denotes the experiment. Curve a' shows the result for the MS processes involving only the partial p wave.

III. RESULTS AND DISCUSSION

The calculated metal K XANES spectra of KMF$_3$ are compared with the experimental spectra observed by Shulman *et al.*[1] in Figs. 1–5 for M =Mn, Fe, Co, Ni, and Zn. The origin of the energy in these figures corresponds to the MT zero. Before discussing our results, we should like to mention the interpretation of Shulman *et al.* based on comparison between the calculated and measured values of the peak energies. The first weak absorption (labeled A') is assigned to the $1s \rightarrow 3d$ transition since it is observed in all but KZnF$_3$, which has no empty $3d$ orbital. The second absorption (labeled A), present either as a shoulder or a peak, is assigned to the $1s \rightarrow 4s$ transition, the intense absorption peak (labeled B) to the $1s \rightarrow 4p$ transition, and the following peak (labeled C) to the $1s \rightarrow 5p$ transition.

From our figures it is seen that all the calculated spectra are in good agreement with the experiment, although the first very small A' and weak F peaks do not appear in the calculations. The first small peak A' results from a transition to a final bound state, and the calculation of bound-state transitions cannot be carried out by our program. In the calculation the prominent peak B is enhanced, while peak A is generally suppressed. In addition, the weak peak F observed in KMnF$_3$, KFeF$_3$, and

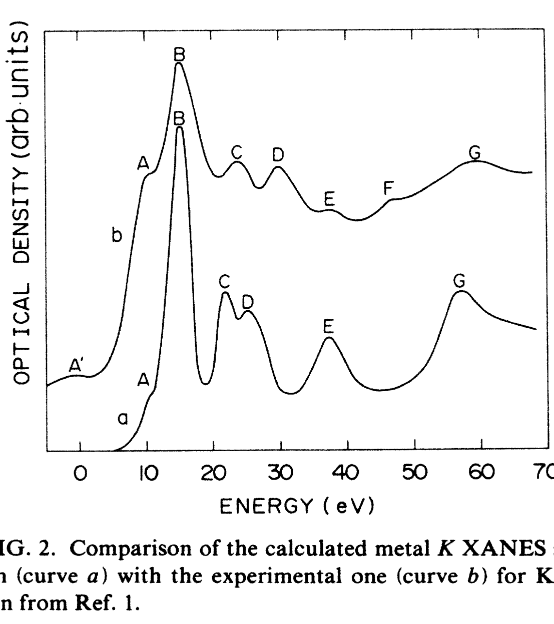

FIG. 2. Comparison of the calculated metal K XANES spectrum (curve a) with the experimental one (curve b) for KFeF$_3$ taken from Ref. 1.

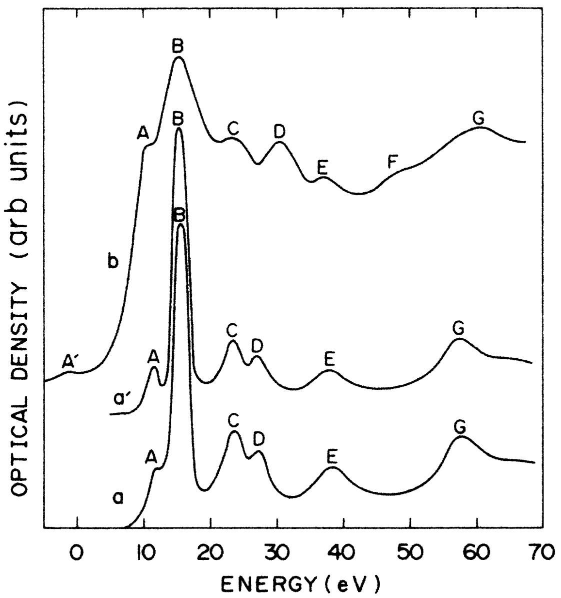

FIG. 3. The same as Fig. 2 but $KCoF_3$. The spectrum calculated by using the crystal potential constructed from neutral atoms is also shown by curve a'.

$KCoF_3$ cannot be predicted. As mentioned in Sec. II, the choices of the MT radii R and MT zero V_0 are not unique. It may be that another choice of them leads to better agreement between calculation and experiment. However, this search was not undertaken because of the large computer time required.

Here let us discuss the relationship between the assignment of atomic states made by Shulman *et al.*[1] and the results of the present calculations. In order to do so, we have made a calculation under the condition that $(l_{\max}, S_{\max})=(1,4)$ and the phase shift of the partial s wave is set to zero intentionally. This calculation corresponds to the situation in which the MS processes involving only the partial p wave occur. The result for this special case is shown in Fig. 1 by the curve a' in the energy region which we are concerned with. This spectrum consists of two peaks in this region, and the two peaks clearly correspond to peaks B and C in curve a. Therefore we can say that peaks B and C in our result have the p character. In curve a' the peak, which should correspond to peak A in curve a, does not appear. Peak A is considered to originate from the scattering of the partial s wave, since the partial cross section of the d wave is negligibly small in this energy region. The assignment of Shulman *et al.* in terms of atomic states is not contradictory to the physics involved in the MS theory.

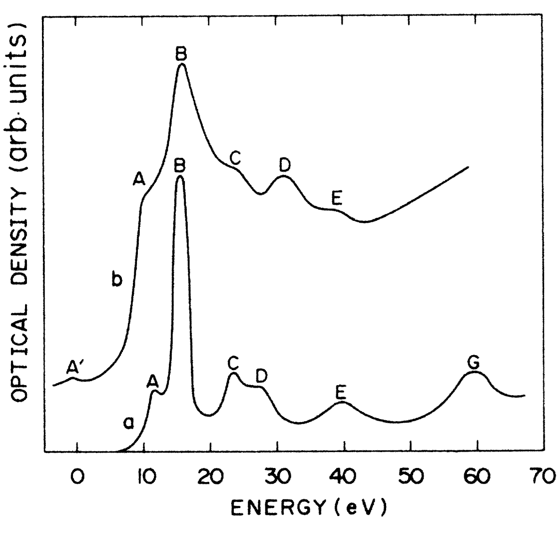

FIG. 4. The same as Fig. 2 but for $KNiF_3$.

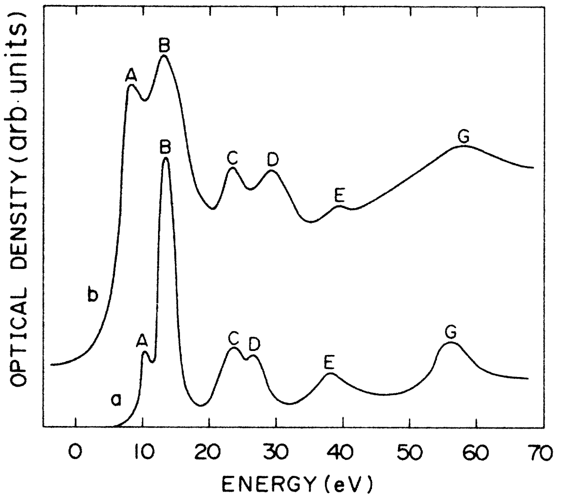

FIG. 5. The same as Fig. 2 but for $KZnF_3$.

Finally, we have examined how the calculated spectrum changes when we adopt the crystal potential constructed from neutral atoms neglecting the charge transfer. $KCoF_3$ was taken as an example. Its result is shown in Fig. 3 by the curve a'. The calculation involves the core hole effect as the case of the other calculations. Only a slight difference is seen around peak A. It follows that the effect of the charge transfer on the metal x-ray-absorption spectrum for KMF_3 is not noticeable. For a system for which it is too complicated to evaluate the Madelung corrections, the so-called high-T_c superconductive multicomponent ceramics, for example, crystal potentials made by neglecting the charge transfer might be used as the potential for the MS calculation of XANES.

At the end we should point out that very recently XANES of $La_{2-x}(Ba,Sr)_xCuO_4$ superconductors were measured,[14,15] and the theoretical calculations for Cu K XANES were done on the basis of a discrete variational method.[15]

ACKNOWLEDGMENT

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