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Extended Fine Structure in X-Ray Absorption Spectra of Certain Perovskites

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In this paper we attempt to test the validity of the short-range-order (SRO) and the long-range-order (LRO) theories of the extended fine structure (EFS) in x-ray absorption spectra. This is done by comparing the EFS's of Ti, Ca, Zr, and Sr in the perovoskitelike compounds $SrTiO_3$, $CaTiO_3$, $SrZrO_3$, and $CaZrO_3$. The regularities which have been anticipated from SRO or LRO theories have not been observed. We are thus led to suggest that models are required other than those which have been used to explain the EFS.

I. INTRODUCTION

There is as yet no acceptable explanation of the extended fine structure (EFS) in x-ray absorption spectra. At present, two basically different theories attempt to explain this effect. The long-range-order (LRO) theory, introduced by Kronig,[1] attributes the EFS in crystals to the band structure of electronic energy levels. Qualitatively, this view correctly accounts for the relative displacements of the EFS extrema in crystallographically similar metals as well as for the similarity of EFS for the K edges of the components of certain binary compounds.[2]

Other experimental results are not easily reconciled with an LRO picture. The difficulty for an LRO-based theory of EFS is evidenced by the occasionally limited range of EFS (in some cases 50 eV or less[3]) and the more than occasional dissimilarities in the EFS for two elements in a compound. The latter becomes especially evident in this work. As may be inferred from the absence of any profile calculations in the literature, models of this class do not easily yield to quantitative treatment.

The other point of view, the short-range-order (SRO) theory,[4] is that the EFS exists primarily because the near neighbors of the absorbing atom influence the transition probability of the photo-ejected electron. Many features of the EFS which are believed to be capable of distinguishing between the two views are, on closer inspection, common to both. (For example, the dependence of the location of the characteristic absorption extrema on the inverse square of the dimensions of the cell is shared by SRO and LRO. Indeed this would follow even if the fine structure were due to recoil of the core electrons plus nucleus.) Qualitative successes for the SRO picture are found in the similarity of spectra in crystalline and amorphous phases, and in the component spectra of certain binaries.

Qualitative difficulties for a typical SRO-type description can be found in the spectra of polyatomic molecules, where this description should be applicable without reservation. It appears that in some cases[5] this expectation is realized, while in others[6] it is not. On the other hand, the SRO picture is readily quantified and has enjoyed semiquantitative agreement with experiment in a number of pure metals, albeit with the aid of some

relatively free adjustments of the scattering phase-shifts.

We have sought to test the SRO versus LRO question on a qualitative level in order to avoid questions arising from the degree of such approximations as are necessarily involved in the quantitative treatment of either model. To this end, we have recorded the EFS of the K-absorption edges of Sr, Ca, Zr, and Ti in $SrTiO_3$, $SrZrO_3$, $CaTiO_3$, and $CaZrO_3$. All the data were obtained at room temperature. At this temperature $SrTiO_3$ has a perfect perovskite structure, and the other materials approximate this structure[7] so closely that in comparing the absorption curves in this family of structurally similar ABO_3 compounds no allowance has to be made for their deviation from the perovskite structure. If LRO were responsible for the EFS, then the A spectrum would tend to be similar to the B spectrum in the same compound. In contrast, the SRO theory predicts similarity between all the A spectra as well as similarity between all the B spectra. In our opinion, neither alternative is supported by the data which are presented below.

II. EXPERIMENTAL

Samples were prepared from fine powders precipitated into a plastic matrix; slow evaporation yielded reasonably homogeneous samples. The absorption curve of Sr in $SrTiO_3$ was obtained also with a single-crystal absorber. The uniformity of thickness of the powdered samples was tested by taking x-ray transmission photographs, and by comparing the absorption curves taken in samples of different thickness. In addition, the EFS of Sr in $SrTiO_3$ was obtained, using a powdered sample (effective thickness of 15 μ) and comparing it with the EFS from a single-crystal absorber approximately 100 μ thick. All the powdered samples showed identical EFS, within the limits of the experimental error; the amplitudes of the EFS of Sr from the powdered sample were about 15% lower than those obtained from the single-crystal absorber.

The absorption curves of Sr and Zr were taken with a double-crystal spectrometer[8] set in a mismatched minus position, certain features of which are described in the following paragraphs. Silicon crystals were used in the spectrometer, the first crystal reflecting from a $\{220\}$ plane, the second from a $\{111\}$ plane. This arrangement yielded a full width at half-maximum for the $MoK\alpha_1$ line of 7 sec of arc, corresponding to 7.5 eV.

We call attention to the utility of this unequal crystal minus position to obtain reduced resolving powers, using a particular crystal species with a concomitant gain in counting rate. The resolving power of any diffraction arrangement is directly proportional to the dispersion and inversely proportional to the diffraction width. There is limited freedom regarding width afforded by choice of a diffraction plane. Extreme mismatching approaches the normal (1, +1) double-crystal position in both resolving power and consequent lack of intensity. Close matching of the crystals in a dispersion canceling arrangement allows trading off of superfluous resolving power for intensity.

Continuum radiation was obtained from a Mo target, sealed-off diffraction tube, operated at 40 kV and 20 mA. Radiation passed through the monochromator was detected by a 1-mm-thick NaI scintillation counter. This was followed by conventional single-channel pulse-height analysis and scaling circuitry. Each absorption curve was obtained by counting point-by-point, with and without the absorber, alternately. The absorption curves of Zr in $CaZrO_3$ and the Sr curves in $SrTiO_3$ were taken by recording 8000 counts and 17 000 counts with and without the absorber, respectively. The absorption curve of Zr in $SrZrO_3$ was taken by recording only 4000 counts with the absorber because of the high Sr absorption in this region. The energy difference between successive points is 1–2 eV, as is shown in Figs. 1 and 2.

The absorption curves of Ti and Ca were taken, using an evacuated double-crystal spectrometer[9] operating in the (1, +1) position. Silicon crystals were used, the reflecting planes being $\{111\}$. The source of continuum radiation was a gold anode operated at 15 kV and 60 mA. The dispersed beam was detected by an argon-methane flow counter operated at approximately one-half of atmospheric pressure. Each absorption curve was taken by scanning the investigated region in steps of 1 eV without the absorber and with the absorber; each curve was determined by counting approximately 10 000 counts without the absorber, and 10 000 4000 counts with it, depending on the absorption of the other components in the sample. Several curves were taken for each absorption edge to check the reproducibility. No corrections were made for background or for the spectrometer window. On the scale of the figures these would be barely visible.

III. RESULTS AND DISCUSSION

The absorption curves in the EFS region of Sr and Ca are shown in Fig. 1, these of Zr and Ti in Fig. 2. The abscissa represents the energy of the x rays. The zero of the abscissa is chosen separately for each element near its apparent absorption edge, but the same zero was taken in the absorption curves of the same element in its two
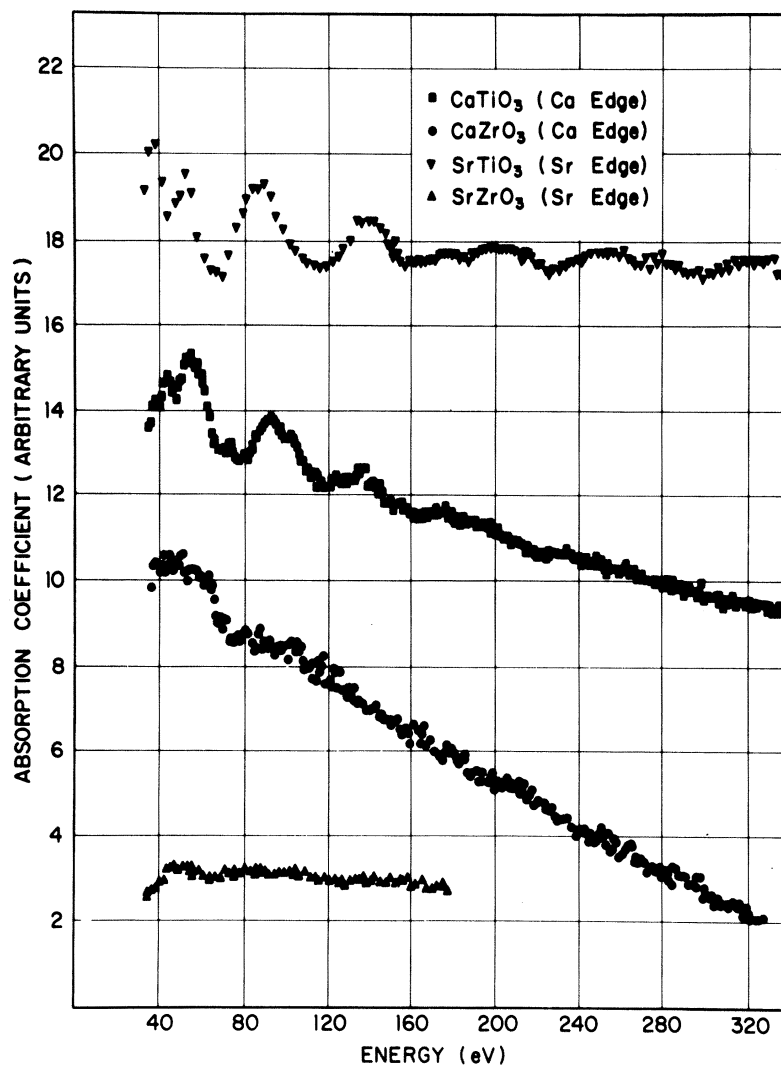
FIG. 1.   EFS of the K edges of Ca and Sr found in the titanate and zirconate of each.   Note that zero on the ordinate scale is considerably and variously suppressed to clarify the region of EFS.

compounds.   The ordinate is proportional to the absorption coefficient.   Figures 1 and 2 have ordinate zero suppression to permit a relatively clear delineation of the variation of absorption coefficient in the region of EFS.   Figure 3, on the other hand, shows the edges themselves in such a way as to indicate relative "chemical shifts" and to show the strong Kossel structure found in some cases.

There is no way to distinguish unambiguously between the Kossel and the extended structures. We shall assume here that the absorption maxima appearing below 40 eV belong to the Kossel structure.   We base this assumption on the width of the low-energy maxima.   The positions of the first few absorption maxima are given in Table I.   The

numbers represent the positions of the maxima as they appear in Fig. 3.   The widths of these absorption maxima are not given in the table, since owing to their overlap it is not possible to determine them.   However, Fig. 3 shows that below 45 eV the maxima in the absorption curves of Sr in $SrTiO_3$, of Ca in $CaTiO_3$, and of $CaZrO_3$ are very narrow in comparison with the maxima at higher energies.   In fact, their width is smaller than the width deduced from the SRO theory [Eq. (1)].   Noting that absorption maxima of the Kossel structure are narrower than the EFS maxima, and the fact that the absorption curve of Sr in $SrZrO_3$ levels off at 45 ± 2 eV, we attribute the absorption maxima appearing in Fig. 1 below 40 eV to the Kossel structure.   There is no observed Kossel structure

on the Sr absorption curve in $SrZrO_3$. This is not understood, but the structure might be smeared out by the nonuniform stresses in the $SrZrO_3$ crystal on the sites of the Sr atoms. Similar arguments make us believe that the narrow absorption maxima on the Ti absorption curves (i. e., the maxima up to 40 eV in Fig. 3) and the first absorption maxima on the Zr absorption curves belong to the Kossel structure. The large extent of the Kossel structure in this case is probably due to the high ionicity of the Ti and Zr atoms in these perovskites.

We now show that our results are not compatible with the LRO theory. The LRO theory predicts that in each of the investigated ABO_3 compounds the EFS of the A atoms is similar to that of the B atoms. The number of the EFS extrema and their relative positions on the absorption curves of the A's and B's must be the same. Differences between the EFS at the K-absorption edges of the A atoms and those of the B atoms may appear, due to two effects: (i) The crystal potential at the sites of the A and B atoms are different, and (ii) the A and B atoms have different ionicities. Both effects, however, influence neither the number of

the EFS extrema nor their relative positions on the absorption curves, which are determined entirely by the band structure in the ABO_3 compound. Comparison of the respective absorption curves, presented on Figs. 1 and 2, shows that the expected similarity is not realized.

Another point is to be made: According to the Kronig theory the EFS in a given compound depends by and large on the width of the forbidden-energy regions in the crystals. Their width is closely related to the corresponding crystal-structure factors.[10] The crystal-structure factors in $SrTiO_3$ are considerably different from those in $CaTiO_3$. This is due to the large differences between the atomic scattering factors of Sr and Ca. Therefore, we should expect the EFS of Sr in $SrTiO_3$ and the EFS of Ca in $CaTiO_3$ to be different. Comparison of the respective curves reveals that, contrary to expectation, there is a pronounced similarity in their EFS. We note also that the ionic charge of Sr in $SrTiO_3$ is 1.85,[11] while that on Ca in $CaTiO_3$ is 1.0.[12] As was pointed out above, this shows that the ionic charge on an atom does not seriously affect the EFS. All these considerations strongly
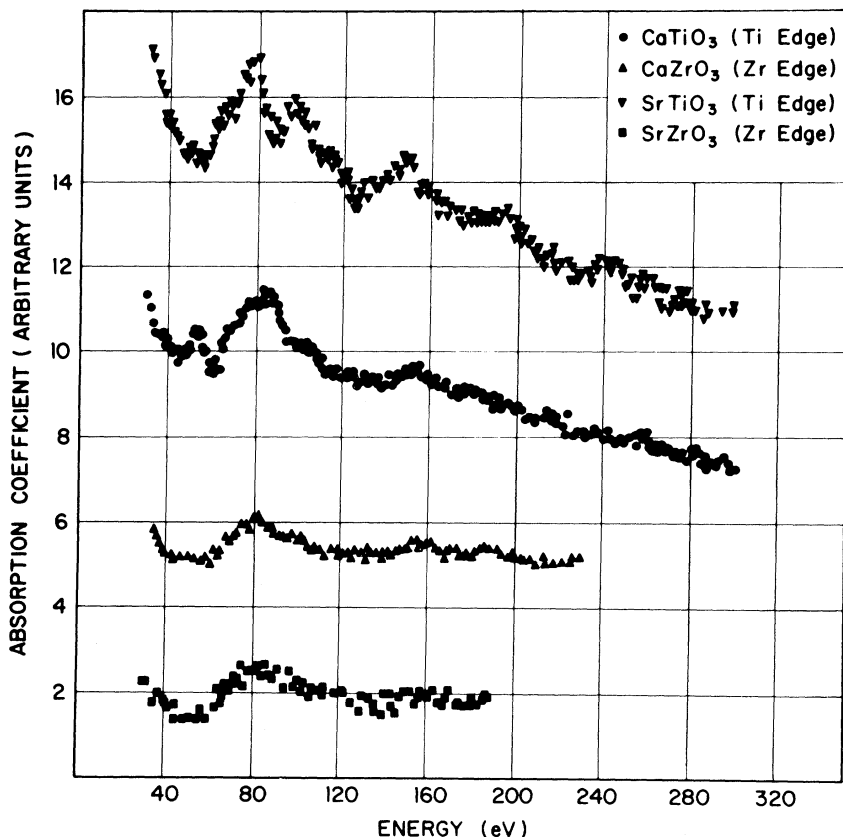

FIG. 2. EFS of the K edges of Ti and Zr as found in the titanates and zirconates of Ca and Sr. Ordinate zeroes are suppressed for clarity of the EFS.
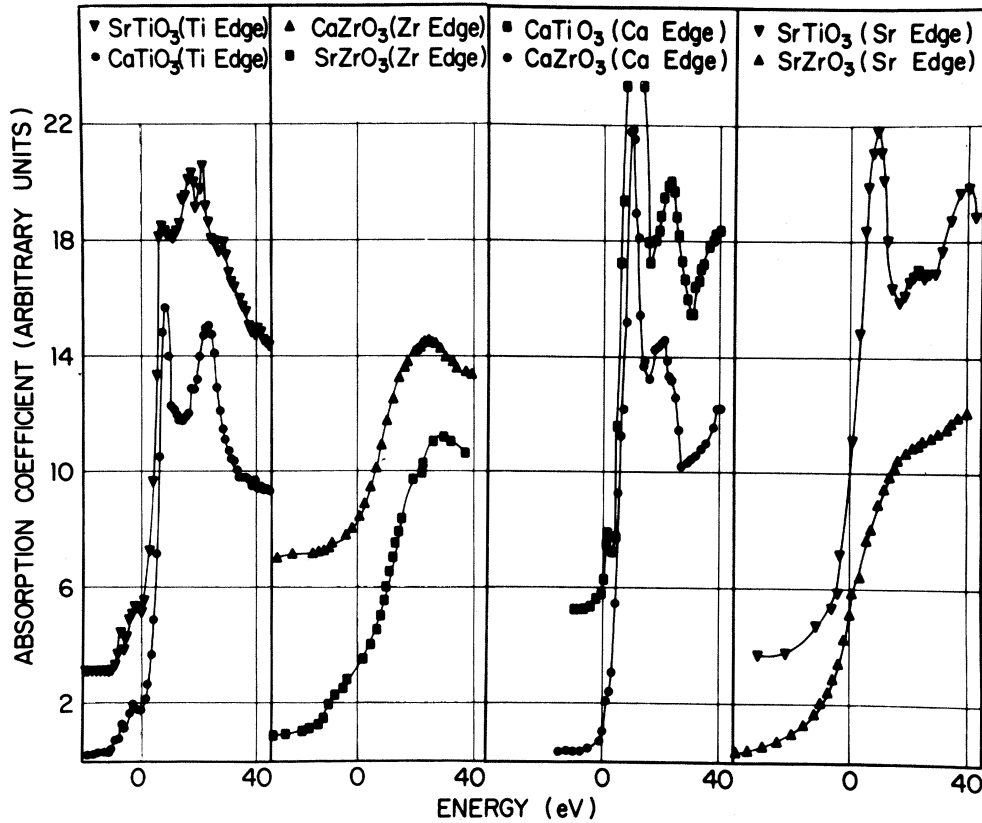
FIG. 3. Initial absorption structures for all edges studied.

suggest that the Kronig theory of the EFS is basically inadequate.

In the following we shall attempt to discuss our results on the basis of the SRO picture. In the framework of the SRO theory the fluctuating part of the K-absorption coefficient $\Delta\tau(E)$ is given, approximately, by the following expression:

$$\Delta\tau(E) = \sum_i A_i(E)\sin(2Kr_i + 2\eta_1), \tag{1}$$

where

$$A_i(E) = \int_{-\infty}^{\infty} \overline{V}_i(x)\cos2Kx\,dx.$$

In this equation E is the energy of the photoelectron. K is the corresponding pseudomomentum, r_i is the radius of the ith-coordination sphere. η_1 is the phase shift due to the field of the absorbing atom for the partial way $l=1$, $\overline{V}_i(x)$ is the average potential (over a sphere centered at the absorbing atom) of the atoms of the ith coordination sphere. This expression for $A_i(E)$ is valid for crystals and molecules with centers of symmetry, and thus obviously for cubic lattices. Equation (1) was derived for metallic crystals[4] by assuming that the potential of the absorbing atom is screened by the

conduction electrons. In this case, η_1 is constant everywhere outside the absorbing atom and determined only by the energy E of the photoejected electron. In ionic crystals such screening does not exist, causing a different dependence of the $\eta_1(E)$ curve.

In the derivation of Eq. (1), the potential of the atoms belonging to one coordination sphere is averaged over this sphere. Therefore, the accuracy of the averaging approximation improves as the number of atoms of one element situated on the coordination sphere increases. In the compounds which we investigated, the different atoms are situated at nonequivalent sites. The oxygens occupy the $(n+\frac{1}{2}, p+\frac{1}{2}, 0)$ positions, the divalent atoms occupy the (n, p, l) positions, and the quadrivalent atoms occupy the $(n+\frac{1}{2}, p+\frac{1}{2}, l+\frac{1}{2})$ positions. Therefore, each coordination sphere holds only one kind of atom. In addition, the coordination number is high so that the above described approximation inherent in Eq. (1) is good.

The relevant features of the absorption curves of the investigated compounds in the EFS region can be summarized as follows: The positions of the observed extrema of Sr and Ca, with the ex-

ception of the maxima at 75 eV (Fig. 1), and of Ti and Zr, with the exception of the absorption maxima at 52 eV (Fig. 2), are nearly coincident. The extent of the fluctuations in the different absorption curves varies greatly. For Sr in $SrTiO_3$ it is as high as 300 eV, while there are no observable fluctuations in the absorption curve of Sr in $SrTiO_3$. The fluctuations in the other absorption curves have intermediate ranges.

The SRO theory attributes the difference in the EFS in metals and insulators to the screening of the ionic potential by the conduction electrons in the metals. In contrast, in insulators the ionic charge produces a long-range field which causes the phase shifts η_1 to change even at large distances from the absorbing atom. Therefore, in the insulators $\eta_1 = \eta_1 (E, e, r_i)$, where e is the ionic charge on the absorbing atom. Thus the relative positions of the extrema must depend on the ionic charge on the absorbing atom. In addition, the phase shift also depends strongly on the atomic number. Such dependence is not apparent in the materials which we investigated. Figure 1 shows that the separations of the successive EFS absorption extrema in the absorption curves of Sr in $SrTiO_3$ and of Ca in $CaTiO_3$ are nearly the same, although the charges in these compounds on the Sr and Ca atoms are $+1.85$[11] and $+1.0$,[12] respectively. It is also worth noting that the extent of the EFS of Sr in $SrTiO_3$ is larger than that of Ca in $CaTiO_3$. According to the SRO theory, we would expect an opposite effect due to the higher charge in the Sr atom.

$SrZrO_3$ has a distorted perovskite lattice. Its tolerance factor is $t = 0.91$.[13] The high value of the tolerance factor and the small splitting of the diffraction lines indicate that the distortion is not larger than that in $CaTiO_3$ ($t = 0.89$) and in $CaZrO_3$ ($t = 0.84$). Therefore, the absence of the EFS of Sr in $SrZrO_3$ cannot be attributed to the displacements of the atoms from their corresponding perovskite sites.

No phase transitions have been reported in

$SrZrO_3$; therefore, no unusually high-amplitude lattice vibrations are present to wash out the EFS. The absorption curve of Zr taken with the same sample is not flat (Fig. 2), which demonstrates that the sample quality is adequate to observe such structure. It was noted that the absence of the Kossel structure in the Sr absorption curve of $SrZrO_3$ might be attributed to a very strong deformation of the crystal field, at the site of the Sr atom. Such deformation cannot account for the absence of the EFS, since no EFS is observed in the Ca absorption curve in $CaZrO_3$, which shows a very pronounced Kossel structure. We are led, therefore, to attribute the absence of the EFS of Sr in $SrZrO_3$ and of Ca in $CaZrO_3$ to the fundamental aspects of the mechanism underlying the EFS.

The integrand in Eq. (1) involves the potential at the site of the scattering atom. Therefore, on the basis of the SRO theory, it seems plausible to expect a higher contribution to the EFS from the Zr atoms in $SrZrO_3$, than from the Ti atoms in $SrTiO_3$. This is contrary to observations.

We note that in the EFS region the separation between successive absorption maxima for Sr in $SrTiO_3$ are approximately the same as those between the corresponding absorption maxima for Ca in $CaTiO_3$ (Fig. 1). A similar situation exists also with respect to the absorption curves of Ti in $SrTiO_3$ and Zr in $CaZrO_3$ (Fig. 2). As discussed below, this is contrary to what one would expect from the SRO model. In the SRO model the equal separations between the corresponding absorption maxima would imply identical phase shifts. Thus, according to this model the phase shifts $\eta_1(E, e, r_i)$ are the same for the Sr and Ca atoms, as well as for the Zr and Ti atoms. It has been noted above that the phase shifts depend upon the atomic numbers. In the case of short-range fields, as in metals, $\eta_1(E)$ is approximately proportional to $\sqrt{Z}$. Within the electronic shells the electrostatic field acting on the photoelectron is similar in ionic crystals and in metals because the conduction electrons

TABLE I. Positions of low-energy absorption maxima of Sr, Ca, Ti, and Zr in $SrTiO_3$, $SrZrO_3$, $CaTiO_3$, and $CaZrO_3$.[a]

Absorbing element	Sample	Positions of low-energy maxima in eV as given in Figs. 1 and 2[b]								
Sr	$SrTiO_3$			8.5+1	22.5±1	39.5±1	44.5±2	55±1		
Sr	$SrZrO_3$									
Ca	$CaTiO_3$	1±0.5		9±0.5	22±1	39±1	44.5±2	55±2		
Ca	$CaZrO_3$			8±0.5	20±1					
Ti	$SrTiO_3$	−7±0.5	−2±0.5	7±1.5		17±1.5	21.5±1.5	28±1	40±1	50±2
Ti	$CaTiO_3$	−7±0.5	−2.5±0.5	8±1		17±1	23±1		37±2	52.5±2
Zr	$SrZrO_3$							29±2		
Zr	$CaZrO_3$							24±2		

[a]Entries are arranged so as to emphasize numerical correspondence noted in various compounds of the same element.
[b]Indicated uncertainties are intended to reflect estimates of over-all error.

hardly penetrate the electronic shells. Therefore, we may approximate the phase shifts in ionic crystals at a distance r outside the absorbing atom by $\eta_1(E,\ e,\ r) = \eta_1'(E) + \eta_1'(E,\ e,\ r)$, where $\eta_1'(E)$ is proportional to $\sqrt{Z}$ and $\eta_1(E,\ e,\ r)$ depends on the ionic charge of the absorbing atom. We would then expect different phase shifts in Sr and Ca, as well as in Zr and Ti atoms.

IV. CONCULSIONS

Neither of the EFS theories discussed here can account for even the "gross" characteristics of the absorption spectra in the investigated perovskites. The Kronig theory is definitely rejected owing to the similarity of the Ti K-absorption curves in $SrTiO_3$ and $CaTiO_3$. The SRO theory also seems to be inadequate. However, our results are not as conclusive with respect to this theory as they are with respect to the Kronig theory. The equal separation of the successive maxima can be explained by assuming that in the relevant energy interval the first derivatives of the phase shifts with

respect to the energy of the photoelectron are equal. Neither calculations of the phase shifts nor their independent experimental determinations are available for the compounds which we investigated. However, the required dependence of the phase shifts on energy in an energy region of the order of 200 eV is generally not expected from the theory.[14] Nevertheless, it is not completely out of the question. The absence of the EFS in Sr and Ca in $SrZrO_3$ and $CaZrO_3$, respectively, would here be attributed to destructive interference of the scattered photoelectron wave function over all the investigated energy region. Again it is highly improbable that this will happen over a 200-eV interval. We also note that there is a difference in the literature between the definitions of the ionic charges on the Sr atom in $SrTiO_3$ and the Ca atom in $CaTiO_3$ (Refs. 11 and 12), which limits the meaningfulness of the comparison. The inability of the existing theories to conform to the observed EFS suggests that it is desirable to look for rather different mechanisms to explain this effect.

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