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Near-Edge Fine Structure and Metal K Edges
of LaFeO₃ and LaCoO₃**

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Theoretical analysis of x-ray-absorption near-edge fine structure at the O and metal K edges of LaFeO_3 and LaCoO_3

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We present experimental x-ray-absorption spectra at the oxygen and 3d transition-metal K edges of LaFeO_3 and LaCoO_3 . We interpret the experimental results in terms of detailed theoretical calculations based on multiple-scattering theory. Along with providing an understanding of the origin of various experimental features, we investigate the effects of structural distortions and the core-hole potential in determining the experimental spectral shape. The results indicate that the core-hole potential as well as many-body effects within the valence electrons do not have any strong effect on the spectra suggesting that the spectral features can be directly interpreted in terms of the electronic structure of such compounds. [S0163-1829(97)05028-5]

I. INTRODUCTION

Electronic structures of 3d transition-metal oxides exhibit a wide range of electronic properties including insulating, metallic, and superconducting ground states; these compounds also have varied magnetic properties.¹ Many of these systems show interesting electronic and magnetic phase transitions as a function of temperature, pressure, or charge carrier doping. Recently, there has been a particular resurgence of intense activity in investigating the electronic and magnetic properties of these systems following the discoveries of many exotic properties in this class of system, such as high-temperature superconductivity,² colossal magnetoresistance effects,³ and other phenomena indicating a close interplay between electronic, magnetic, and structural properties. Various forms of high-energy spectroscopies, such as photoemission, inverse photoemission, and x-ray-absorption spec-

troscopies, have played very important roles in our understanding of the electronic properties of these fascinating materials by providing microscopic information related to the various single-particle excitation properties.⁴ However, it is often necessary to interpret these results in conjunction with some suitable theoretical analysis in order to obtain information about the ground-state properties of these materials. Such analyses have been carried out extensively particularly in the context of the photoemission spectroscopies, though theoretical analyses of x-ray-absorption (XAS) spectroscopic results are very few. On the other hand, x-ray-absorption spectroscopy is particularly useful in obtaining electronic-structure information in many of the systems exhibiting metal-insulator transitions in the presence of hole doping.⁵ This is due to the fact that such hole-doped states appear in the unoccupied part of the spectrum, which is most suitably probed by x-ray-absorption spectroscopy.

There are several issues involved in extracting electronic-structure information from experimental x-ray-absorption spectra of transition-metal oxides. We discuss some of these aspects in the following.

(1) It is well known that the various properties of these transition-metal oxides are often crucially connected with the geometric structures, such as structural distortions around the transition-metal sites.^{6,7} However, the analysis of spectroscopic data has often been described in terms of idealized structures possessing higher symmetries.⁸ Based implicitly on the assumption that these small structural distortions do not have any observable effects on the spectroscopic properties, such procedures considerably reduce the theoretical complications involved. However, the justifiability of such assumptions has not been verified explicitly so far.

(2) Since the final state of the absorption process, which solely determines the energy spectrum of the experimental observation, has a core hole, core-hole potential effects in principle can distort the experimental spectrum considerably compared to the ground-state electronic structure. However, most of the recent analysis of XAS, particularly at the oxygen *K* edge of the transition-metal oxides,⁹ has not taken into account the possible effects of core-hole potential. This is not *a priori* justifiable since the core-hole potential is known to have a profound influence on the XAS spectrum of various systems,^{10,11} including XAS at the *K* edge of oxides.¹²

(3) While the core-hole potential has been ignored in the analysis of the XAS spectrum as discussed above, most of the analysis of experimental spectra in the recent past has been performed within model many-body Hamiltonian approaches that emphasize strong intra-atomic Coulomb interaction, often involving detailed multiplet interactions within the transition-metal *d* manifold.⁹ It is obvious that in the presence of substantial influence of such many-body effects on the experimental spectra, it is not possible to directly relate the spectral features to the ground-state electronic properties since electron correlation effects strongly modify the spectral distribution in the final state of the absorption process. Thus it becomes absolutely necessary to analyze the spectroscopic information in conjunction with detailed many-body calculations in order to obtain ground-state information. In contrast, it has been shown recently^{6,13} that single-particle excitation spectra from the transition-metal oxide systems under discussion here can be described reasonably well in terms of *ab initio effective single-particle* theories. This latter approach has the advantage that the observed spectroscopic features can be related directly to the ground-state properties and thus leads to a considerably more transparent and direct interpretation. However, the situation with respect to x-ray-absorption spectra *vis-à-vis* the influence of electron correlation effects has not been settled yet, though one work has reported a limited agreement between the experimental spectra and single-particle theories.¹³ In this latter work, an *ad hoc* contraction of the energy axis had to be introduced as a fitting parameter; moreover, the intensity variation in the calculated spectrum over a wide energy range was not in good agreement with the experimental spectrum.

We present here a detailed theoretical analysis of experimentally obtained XAS spectra at the *K* edges of the transition metal as well as the oxygen for two typical transition-

metal oxides LaFeO₃ and LaCoO₃ with the perovskite structure in order to address the above-mentioned issues. Furthermore, the present results also indicate the small but finite influence of various structural distortions in determining the spectral details. Calculated results including and excluding the core-hole potentials help to establish that the influence of the core hole in the XAS spectra of these compounds is indeed small, in contrast to many other cases of pronounced core-hole potential effects.^{10,12} Moreover, the present calculations based on single-particle theories provide remarkably accurate descriptions of the experimental spectra in terms of both energy positions of various features and their relative intensities without any adjustable parameter, suggesting that electron correlation effects including multiplet interactions do not influence the spectroscopic properties in these compounds to any significant extent. These two points together would allow a direct interpretation of the x-ray-absorption spectra from these and similar compounds in order to understand the ground-state electronic structures.

II. EXPERIMENT

The samples were prepared by solid-state reactions of stoichiometric quantities of La₂O₃ with CoC₂O₄·2H₂O or FeC₂O₄·2H₂O following the procedures of Ref. 14. The x-ray-absorption spectra at the oxygen *K* edge were obtained at the SX700-I beamline at BESSY, Berlin, in the total electron yield mode. The total resolution¹⁵ for these spectra was about little smaller than 1.0 eV. XAS measurements at the Fe and Co *K* edges were performed at the GILDA CRG(D8) bending magnet beamline of the European Synchrotron Radiation Facility in Grenoble, France. We used a double-crystal monochromator mounting Si(311) crystals and with sagittal focusing. The spectra were measured in the transmission mode with Ar-filled ionization chambers and the overall resolution¹⁶ is estimated to be around 0.7 eV. The samples were prepared by ball milling the fine grain powders with N₂B and then compressing to obtain homogeneous samples, which were kept at the liquid-nitrogen temperature during the experiment.

III. THEORETICAL DETAILS

Our calculations are based on one-electron multiple-scattering theory.¹⁷ The Coulomb part of the potential is built by following the Mattheiss prescription¹⁸ by superimposing neutral-atom charge densities obtained from the Clementi-Roetti table and the Hermann-Skillman wave functions for heavy atoms ($Z > 54$). This method, in general, is known to provide charge distributions quite close to those obtained by self-consistent calculation for metallic and covalent systems (see Ref. 17). For the exchange-correlation part of the potential we use the real Hedin-Lundqvist (HL) self-energy.^{19,20} The calculated spectra are further convoluted with a Lorentzian function with a full width of $\Gamma_r \approx 1.0$ eV for oxygen and 2.0 eV for metal to account for the core-hole lifetime and experimental resolution.²¹ We have chosen the muffin-tin radii according to the Norman criterion²² and have allowed a 10% overlap between contiguous spheres to simulate the atomic bond. The *z* axis in all our calculations is along the *c* axis of the compounds.

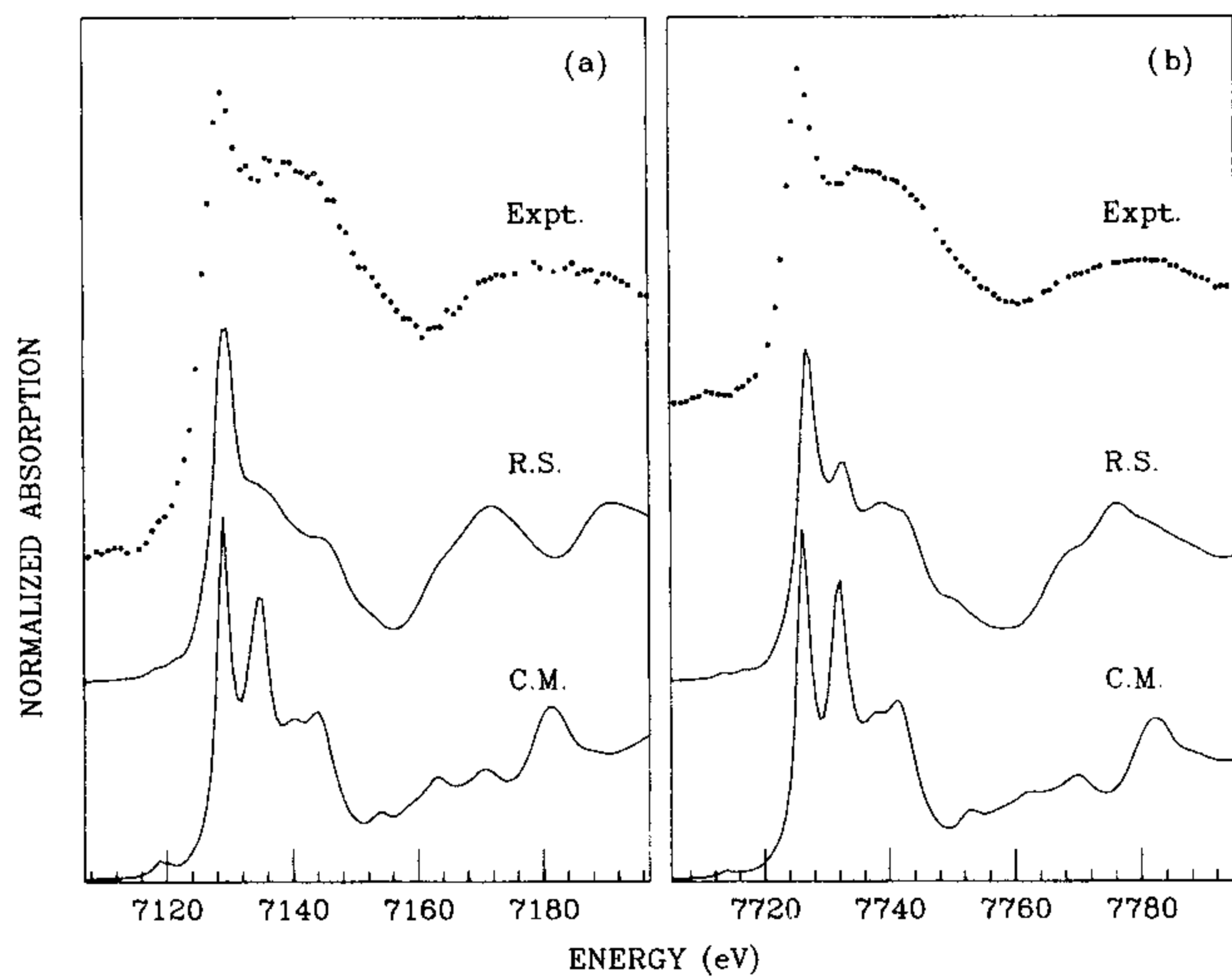


FIG. 1. Comparison between experimental data (dots line) and multiple-scattering calculated XAS spectra for (a) LaFeO_3 and (b) LaCoO_3 at the metal K edges by using the distorted real structures of Refs. 27 and 28 (curve R.S.) and the idealized cubic model of Ref. 26 (curve C.M.).

Density of states (DOS) calculations were performed using density-functional theory within the local-density approximation. For solving the one-electron Schrödinger equation self-consistently we used the tight-binding representation of the scalar-relativistic linear muffin-tin orbital method using the Andersen program. More details can be found in Refs. 23 and 24.

IV. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b), we show the experimental transition-metal K -edge XAS spectra from LaFeO_3 and LaCoO_3 , respectively. The spectra appear to be similar between the two compounds arising from the fact that the two compounds have similar geometrical structures. The metal edges are dominated by the contribution coming from the first-shell atoms giving rise to the typical fine structures common to transition-metal oxides with octahedral coordinations.²⁵ While differences in the details of the band structures between the two compounds are expected to give rise to some differences in the first few electron volts of the absorption thresholds, strong broadening of the experimental spectra due to substantial core-hole life-time broadenings smear out such details in these cases. We performed real HL calculations for both compounds using two different structural models: the idealized cubic perovskite model²⁶ (indicated in the figures by C.M.) and another model that takes into account all the distortions of the real crystal structures (indicated in the figures by R.S.) of LaFeO_3 (Ref. 27) and LaCoO_3 .²⁸ The results obtained with multiple-scattering calculations for these two models are also shown in Figs. 1(a) and 2(b) for LaFeO_3 and LaCoO_3 , respectively. Results in Fig. 1 clearly show that the calculations based on the undistorted idealized cubic structures suggest considerably more structured features for both the compounds compared to the experimental curves, not only close to the threshold energies, but also very far above it. For example, the calculation based on the idealized structures produce a two-peak structure with

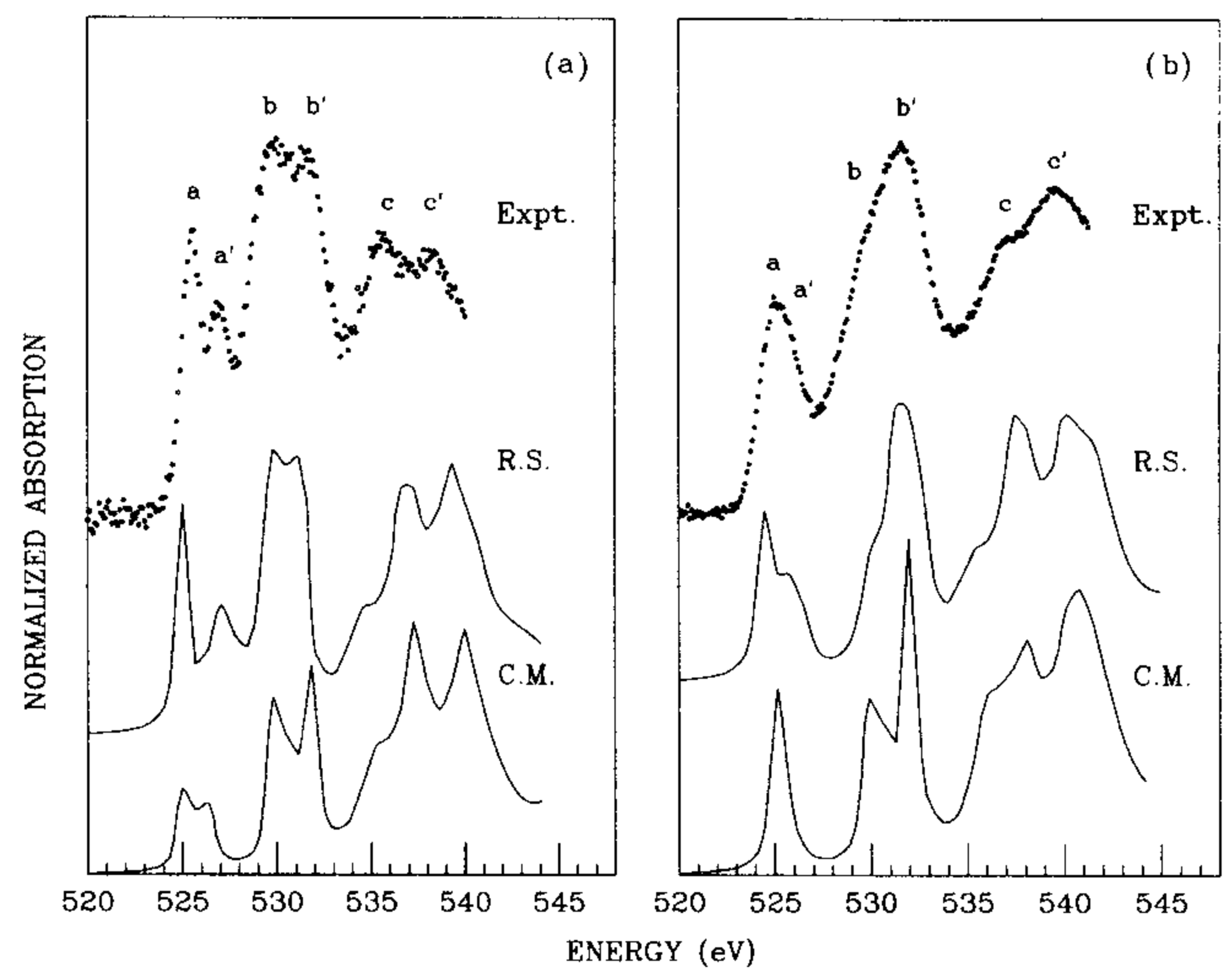


FIG. 2. Comparison between experimental data (dots) and multiple-scattering calculated XAS spectra for (a) LaFeO_3 and (b) LaCoO_3 at the oxygen K edge by using the distorted cubic model of Refs. 27 and 28 (curve R.S.) and the idealized cubic model of Ref. 26 (curve C.M.).

nearly equal intensities near the threshold energies for both the compounds, whereas the experiments show only a single sharp feature. The calculated results for the real structure (RS) are in much better agreement with the observed results in this regard. Likewise, the calculated results with ideal cubic model (CM) structure exhibits a narrow single prominent peak about 50 eV above threshold, while the experimental results suggest superposition of several peaks of comparable intensities giving rise to a broad feature. This is once again in better agreement with the calculated RS results using the real structures. These results clearly suggest that the structural distortions play an important role in determining the details of the electronic structures of these transition-metal perovskite oxides.

In Figs. 2(a) and 2(b), we show the corresponding results for the oxygen K edges in these two compounds. The experimental spectra for the two compounds show considerable differences between the two compounds in this case, in contrast to Fig. 1, reflecting the differences in the electronic structures of the two compounds. This arises from the fact that the lifetime broadening in the oxygen $1s$ core-hole state is considerably smaller than that in the transition-metal $1s$ core-hole state. In the case of the oxygen K -edge spectra also, we find that the calculations based on the idealized cubic structures are in poor agreement with the experimental results for both the compounds, particularly in the near-threshold features. For example, the idealized CM calculation for LaFeO_3 yields a doublet structure of two peaks of nearly equal intensity, whereas the leading feature is much more dominant in the experiment. This is correctly described by the RS calculation. Similar discrepancies can also be seen in the case of the idealized CM calculation for LaCoO_3 in Fig. 2(b). On the contrary, there is much better agreement between the experimental results and the calculations based on the realistic crystal structures, once again establishing that the structural distortions have finite and observable influences on the spectroscopic properties.

It is to be noted that the x-ray-absorption spectra at the

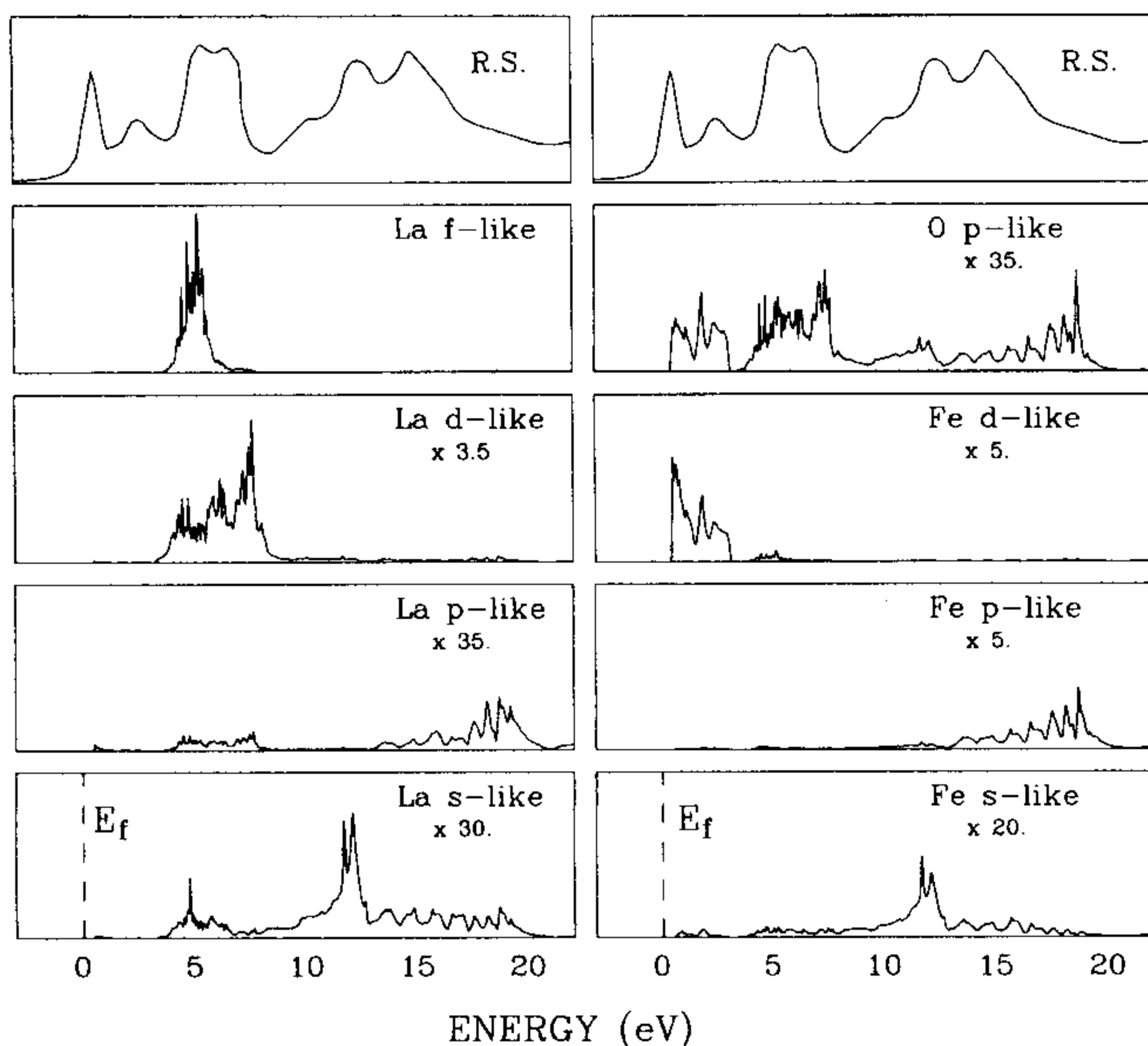


FIG. 3. Site and angular momentum projected density of states relative to the LaFeO_3 system. For comparison, the multiple-scattering XAS spectra related to the distorted cubic model [curve R.S. in Fig. 2(a)] are reported in the uppermost part of the figure. The vertical scales of the DOS calculations are normalized to the La f -like states.

oxygen K edge probe the unoccupied states with the oxygen p symmetry due to the dipole selection rules. These primarily arise from hybridization mixing of oxygen p states with various states of the neighboring atoms. We have analyzed the origin of the various spectral features in the XAS spectra of Fig. 2 by investigating the site and angular momenta projected densities of states for the realistic crystal structures in each case. For brevity, we report in Fig. 3 these partial densities of states only for the LaFeO_3 compound. The other material shows a very similar behavior. These figures show that the spectral features close (approximately 4 eV) to the threshold (marked a and a' in Fig. 2) arise from the covalent or hybridization mixing of the oxygen p states with the transition-metal d density of states. The pronounced doublet feature in the experimental XAS of LaFeO_3 and LaCoO_3 in this energy region is due to the crystal-field splitting of the transition-metal $3d$ level in t_{2g} and e_g levels due to the local cubic field around the transition-metal sites, in agreement with an earlier assignment.¹³ The spectral features marked b and b' in Figs. 2(a) and 2(b) arise from the mixing of oxygen p states primarily with the La d states, while the still-higher-energy features marked c and c' in the figure are due to a similar mixing with the transition-metal s and p and La s states.

There is a close similarity between DOS and cluster calculations, although this is not evident *a priori* because they use different exchange-correlation potentials. However, the local-density exchange-correlation potential in DOS calculations is nothing but that the HL self-energy calculated at or near the Fermi level for occupied states. Due to the slow variation of this latter for states lying in the energy range of about 15 eV above the Fermi level, one can be rather confident that the calculated DOS reflects the one calculated with the true HL potential as in our cluster calculations.

From the above results it is clear that the calculated re-

sults are in good agreement with experimentally observed data of both oxygen and transition-metal K -edge x-ray-absorption spectra of these compounds, when the realistic structural details are taken into account. This is true for both the near edge structures as well as structures considerably higher in energy than the threshold energies. The main discrepancy between the experimental and calculated results appears to be an underestimation of the spectral features; this discrepancy appears to increase systematically for more energetic features. This is indeed to be expected in view of the fact that we have used a fixed lifetime broadening parameter, while it is known that the lifetime width is strongly energy dependent. However, we have not tried to incorporate such a parametrized approach merely to improve the fit since our main purpose here is to show the overall agreement between the results of *ab initio* theory and the experiment. The agreement between the experiment and the calculation for the higher-energy features is not very surprising since correlation effects in these highly excited and extended states are likely to be small. On the contrary, the near-threshold XAS features in transition-metal compounds have been interpreted traditionally⁹ in terms of various parametrized many-body theories that emphasize the correlation effects often including multiplet interactions. The present results based on *ab initio* effectively single-particle theory, however, clearly establish that correlation effects do not have any pronounced influence on these spectral features, in contrast to the usual belief.

It is to be noted that the experimental XAS spectrum represents the energy spectrum of the final state of the system with the intensities of various features determined by the transition-matrix elements. In the final state of the x-ray-absorption process, the system has a core hole. It is not possible to determine *a priori* if the influence of the potential arising from this core hole is sufficient to distort the final-state energy spectrum compared to the ground-state energy distribution of the unoccupied states. It is already well known that XAS spectra at the $3d$ transition-metal $L_{2,3}$ edges is very strongly influenced by such core-hole potential effects;¹¹ similar effects have been observed in several other cases also.^{10,12} On the other hand, such effects always have been assumed to be negligible in the context of the oxygen K -edge spectra from transition-metal oxides. In order to investigate the validity of such approaches, we have performed the XAS spectral calculations based on two different final-state potentials. In one case we calculated the theoretical spectra based on the $Z+1$ approximation that accounts for the core-hole potential in the final state; in the other case we calculated the spectra assuming that the final-state potential is the same as the ground-state potential. The $Z+1$ approximation (final-state rule¹⁷) is used to simulate the relaxation around the core hole in the photoabsorber, of atomic number Z , and consists in taking the orbitals of the $Z+1$ atom and constructing the charge density by using the excited electronic configuration of the photoabsorber with the core electron promoted to an empty orbital. This procedure generates a final-state potential related to the fully relaxed electronic configuration. The results obtained on the basis of these two different approaches to the final-state potentials in the case of LaFeO_3 are shown in Fig. 4. The left panel shows the results of the two calculations for the Fe K edge, while that for the

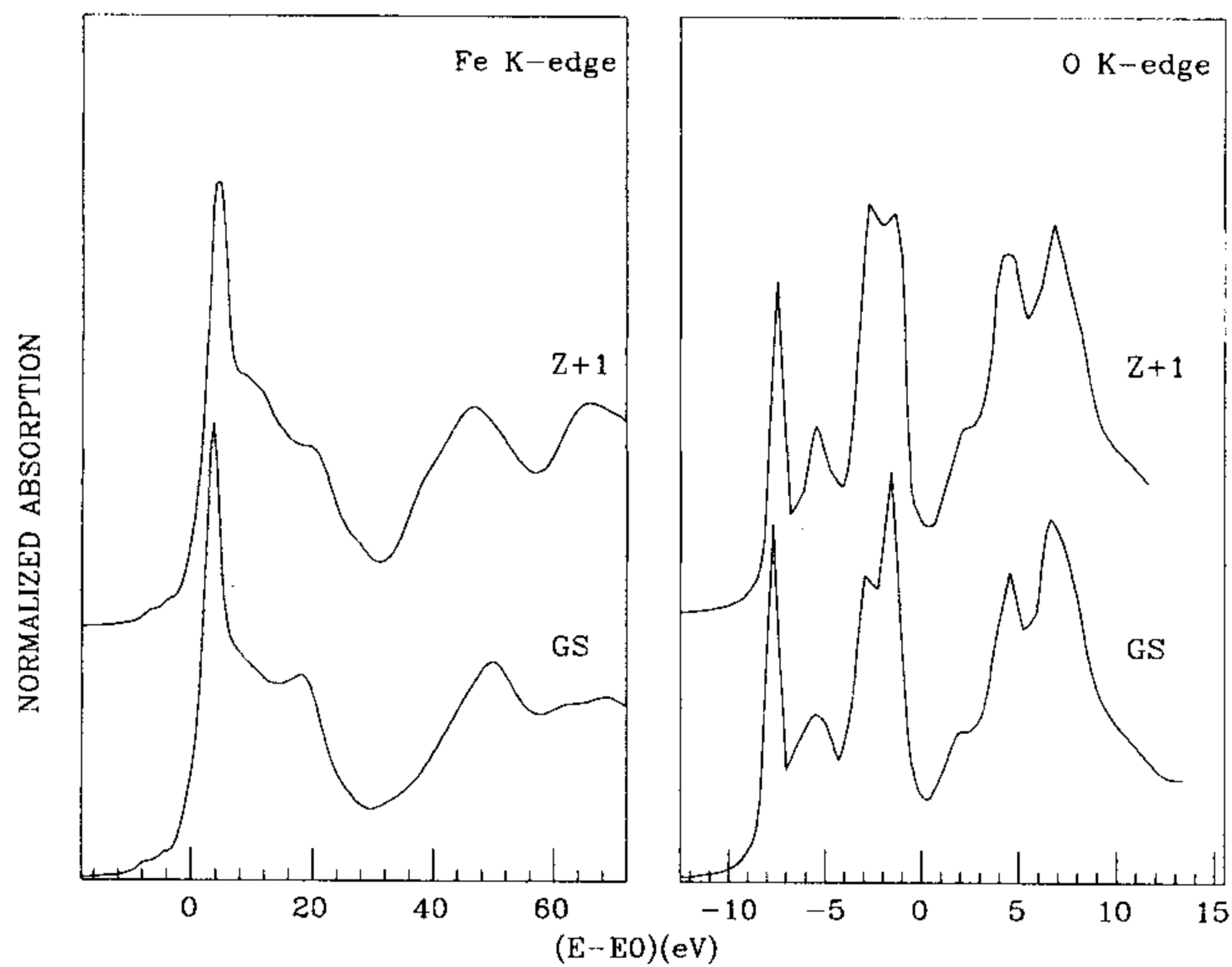


FIG. 4. Comparison between two multiple-scattering calculations of LaFeO_3 at metal (left panel) and oxygen (right panel) K edges obtained using two different final-state potentials: the $Z+1$ final-state potential (upper curves) and the ground-state potential (lower curves).

oxygen K edge are shown in the right panel. The difference between the two calculations, the one with $Z+1$ and the other without, show that there are small changes in the relative intensities of the different peaks, in particular at the O K edge; there is also a slight pulling down in energy of the states in the $Z+1$ calculation. As expected, the calculations based on the $Z+1$ approximation agree better with the experimental results. However, it is interesting to note that the results, except for the small differences mentioned above, are quite similar for the two different approaches. Thus these results clearly establish that the core-hole potential effects are indeed small and can be neglected in qualitative discussions of electronic structures based on transition-metal and oxygen K -edge XAS spectra from such compounds.

V. CONCLUSION

In conclusion, we have presented experimental x-ray-absorption near-edge fine structures at the transition-metal

and the oxygen K edges for LaFeO_3 and LaCoO_3 . These spectra have been compared with the corresponding calculated spectra obtained within the multiple-scattering theory. While the calculations for the idealized cubic structures do not agree well with the experiments, the agreement is substantially improved in the case of the calculations performed with the real crystal structures. This suggests that such structural distortions, often observed in the transition-metal perovskite oxides, play an important role in determining the details of the electronic structures in these systems. The agreement between the experimental results and the calculations based on single-particle theories suggest that correlation effects including multiplet interactions within the transition-metal d manifold do not have any significant influence on the spectral features in these compounds, in contrast to usual wisdom. These *ab initio* theoretical calculations also provide a description of the origin of the various features in the experimental spectra in terms of various hopping interactions between different pairs of states. Furthermore, we have presented theoretical calculations with the final-state potential being described in terms of the $Z+1$ approximation as well as in terms of the ground-state potential. Comparisons of these calculations with the experiments suggest that while there are some small effects on the spectra arising from the core-hole potential in the final state, such effects are generally small in both the transition-metal and the oxygen K edges.

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¹N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1990); N. Tsuda *et al.*, *Electronic Conduction in Oxides*, Springer Series in Solid State Sciences Vol. 94 (Springer-Verlag, Berlin, 1991).

²J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).

³R. von Helmont *et al.*, *Phys. Rev. Lett.* **71**, 2331 (1993); R. Mahendiran *et al.*, *Appl. Phys. Lett.* **66**, 233 (1995).

⁴(a) D. D. Sarma, in *Metal-Insulator Transitions Revisited*, edited by P. P. Edwards and C. N. R. Rao (Taylor and Francis, London, 1995); (b) D. D. Sarma and S. R. Barman, in *Spectroscopy of Mott Insulators and Correlated Metals*, edited by Y. Tokura and A. Fujimori, *Solid State Science* Vol. 119 (Springer-Verlag, Berlin, 1995), p. 126.

⁵J. Garcia, J. Blasco, M. G. Proietti, and M. Benfatto, *Phys. Rev. B* **52**, 15 823 (1995).

⁶D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, *Phys. Rev. Lett.* **75**, 1126 (1995).

⁷S. Satpathy, Zoran S. Popović, and Filip R. Vukajlović, *Phys. Rev. Lett.* **76**, 960 (1996).

⁸A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).

⁹C. T. Chen, L. H. Tjeng, J. Kwo, H. L. Kao, P. Rudolf, F. Sette, and R. M. Fleming, *Phys. Rev. Lett.* **68**, 2543 (1992); J.-H. Park, C. T. Chen, S.-W. Cheong, W. Bao, G. Meigs, V. Chakarian, and Y. U. Idzerda, *ibid.* **76**, 4215 (1996); A. Fujimori, J. H. Weaver, and A. Franciosi, *Phys. Rev. B* **31**, 3549 (1985).

¹⁰E. J. Mele and J. J. Ritsko, *Phys. Rev. Lett.* **43**, 68 (1979); A. Nilsson and M. Martensson, *Physica B* **208&209**, 19 (1995); A. B. Kunz *et al.*, *J. Phys. C* **15**, 5037 (1982).

¹¹J. Fink *et al.*, *Phys. Rev. B* **32**, 4899 (1985); J. Zaanen *et al.*, *ibid.* **32**, 4905 (1985).

- ¹²J. Chaboy, M. Benfatto, and I. Davoli, *Phys. Rev. B* **52**, 10 014 (1995).
- ¹³D. D. Sarma, N. Shanthi, and Priya Mahadevan, *Phys. Rev. B* **54**, 1622 (1996).
- ¹⁴A. Chainani, M. Mathew, and D. D. Sarma, *Phys. Rev. B* **46**, 9976 (1992); **48**, 14 818 (1993).
- ¹⁵D. D. Sarma *et al.*, *Europhys. Lett.* **19**, 513 (1992).
- ¹⁶S. Pascarelli, F. Boscherini, F. D'Acapito, J. Hrdy, C. Meneghini, and S. Mobilio, *J. Synchrotron. Radiat.* **3**, 147 (1996).
- ¹⁷P. A. Lee and J. B. Pendry, *Phys. Rev. B* **11**, 2795 (1975); C. R. Natoli *et al.*, *Phys. Rev. A* **22**, 1104 (1980); P. J. Durham *et al.*, *Comput. Phys. Commun.* **25**, 193 (1982); C. R. Natoli and M. Benfatto, *J. Phys. (France) Colloq.* **47**, C8-11 (1986); P. J. Durham, *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, edited by R. Prinz and D. Koningsberger (Wiley, New York, 1988).
- ¹⁸L. Mattheiss, *Phys. Rev. A* **134**, 970 (1964).
- ¹⁹S.-H. Chou, J. J. Rehr, E. A. Stern, and E. R. Davidson, *Phys. Rev. B* **35**, 2604 (1987); M. Benfatto, in *Proceedings of the Second European Conference on Progress in X-Ray Synchrotron Research*, edited by A. Balerna, E. Bernieri, and S. Mobilio (Società Italiana di Fisica, Rome, 1990), p. 3 and references therein.
- ²⁰C. R. Natoli, M. Benfatto, C. Brouder, D. L. Ruiz Lopez, and M. F. Foulis, *Phys. Rev. B* **42**, 1944 (1990); T. A. Tyson, K. O. Hodgson, C. R. Natoli, and M. Benfatto, *ibid.* **46**, 5997 (1992).
- ²¹*Unoccupied Electronic States*, edited by J. C. Fuggle and J. E. Inglesfield, *Topics in Applied Physics Vol. 69* (Springer, Berlin, 1992), Appendix B.
- ²²J. G. Norman, *Mol. Phys.* **81**, 1191 (1974).
- ²³O. K. Andersen, *Phys. Rev. B* **12**, 3060 (1975); O. K. Andersen and O. Jepsen, *Phys. Rev. Lett.* **53**, 2571 (1984); O. K. Andersen, O. Jepsen, and M. Sob, *Electronic Band Structure and Its Applications*, edited by M. Yussouff (Springer-Verlag, Berlin, 1986); O. Jepsen and O. K. Andersen, *Z. Phys. B* **97**, 35 (1995); W. R. Lambrecht and O. K. Andersen, *Phys. Rev. B* **34**, 2439 (1986); P. E. Blöchl, O. Jepsen, and O. K. Andersen, *ibid.* **49**, 16 223 (1994).
- ²⁴H. L. Skriver, *The LMTO Method* (Springer-Verlag, Berlin, 1984); J. C. Fuggle and J. E. Inglesfield, *Unoccupied Electronic States* (Ref. 21), Chaps. 2, 3, and 5.
- ²⁵J. Garcia, A. Bianconi, M. Benfatto, and C. R. Natoli, *J. Phys. (France) Colloq.* **47**, C8-49 (1986).
- ²⁶W. C. Koehler and E. O. Wollan, *J. Phys. Chem. Solids* **2**, 100 (1957); A. Wold and R. Ward, *J. Am. Chem. Soc.* **76**, 1029 (1954).
- ²⁷M. Marezio and P. D. Dernier, *Mater. Res. Bull.* **6**, 23 (1971).
- ²⁸G. Thornton, B. C. Tofield, and A. W. Hewat, *J. Solid State Chem.* **61**, 301 (1986).