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Authors

Hudson, E.

Moler, E.J.

Zheng, Y.

et al.

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July 1993



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**HIGH-RESOLUTION CORE-LEVEL PHOTOABSORPTION
OF ALKALI HALIDES**

E. HUDSON*†, E. MOLER*†, Y. ZHENG†‡, S. KELLAR*†,
P. HEIMANN§, Z. HUSSAIN§,
and D. A. SHIRLEY‡

*Department of Chemistry,
University of California,
Berkeley, California 94720

†Chemical Sciences Division,
Lawrence Berkeley Laboratory,
University of California,
Berkeley, California 94720

§Accelerator and Fusion Research Division,
Lawrence Berkeley Laboratory,
University of California,
Berkeley, California 94720

‡Departments of Chemistry and Physics,
Pennsylvania State University,
University Park, Pennsylvania 16802

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HIGH-RESOLUTION CORE-LEVEL PHOTOABSORPTION OF ALKALI HALIDES

E. HUDSON¹, E. MOLER¹, Y. ZHENG^{1,3}, S. KELLAR¹, P. HEIMANN², Z. HUSSAIN², AND D. A. SHIRLEY³

¹Chemical Sciences Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

²Accelerator and Fusion Research Division, Lawrence Berkeley Laboratory, Berkeley CA 94720.

³Departments of Chemistry and Physics, Pennsylvania State University, University Park PA 16802.

ABSTRACT

The X-ray Absorption Near Edge Structure (XANES) of single-crystal alkali halide salts have been measured at low temperature ($T \approx 80$ K). By employing the electron partial-yield detection technique, spectra of NaF, NaCl, and NaBr were obtained near the sodium K-edge and spectra of LiF, NaF, and KF were obtained near the fluorine K-edge. All spectra showed sharp features at the absorption threshold and broader absorption features extending 50-80 eV above threshold. The high energy resolution of the soft X-rays ($\Delta E/E \approx 4000$) allowed the detection of previously unobserved fine structure, particularly in the near-edge region. The narrow features below and just above threshold are attributed to core-level excitons. The intense, broader peaks further above threshold are assigned to single-electron scattering resonances. An *ab initio* multiple-scattering calculation is used to model the latter effect. Contributions from atomic multi-electron excitations, estimated by a comparison to the K-edge photoabsorption spectrum of Ne in the gas phase, are found to be very small.

INTRODUCTION

X-ray Absorption Near-Edge Structure (XANES) is widely-used for the study of solid-state electronic and geometric structure. As theoretical advances provide a more quantitative understanding of XANES spectra, it is desirable to test theoretical predictions on relatively well-characterized systems. In this work, XANES spectra were measured for a number of single-crystal alkali halide salts. A combination of high energy resolution and low sample temperature allowed the detection of extensive fine structure from below threshold to ≈ 60 -90 eV above the edge. The results are compared with *ab initio* curved-wave multiple-scattering simulations generated by the FEFF code, which was developed by Rehr and coworkers [1,2].

EXPERIMENTAL

XANES spectra were obtained with high energy resolution using soft X-rays from the Lawrence Berkeley Laboratory Spherical Grating Monochromator on Beam Line 6-1 at the Stanford Synchrotron Radiation Laboratory. Photoabsorption spectra of NaF, NaCl, and NaBr were measured near the sodium K-edge using the second and third orders of diffraction. Spectra of LiF, NaF, and KF were measured near the fluorine K-edge using the first order of diffraction. The single crystals were cleaved along the (100) face in the vacuum chamber at pressures of $\approx 5 \times 10^{-10}$ torr. Spectra were measured at $T \approx 80$ K and at room temperature. Absorption of x-rays by the samples was detected by measuring the partial electron yield with a channeltron. Retardation potentials were selected to accept the Auger electrons corresponding to the core level of interest.

RESULTS

The Na K-edge XANES spectra of NaF, NaCl, and NaBr at $T \approx 80$ K are shown in Fig. 1. These spectra agree with earlier measurements made over a narrower energy range at room temperature using polycrystalline films [3]. The NaCl spectrum was also measured previously at low temperature [4], with sharp near-edge structure very similar to that shown here. Fig. 2 shows the F K-edge spectra of LiF, NaF, and KF measured at $T \approx 80$ K. Similar spectra were previously measured on single crystals over a narrower energy range at an unspecified

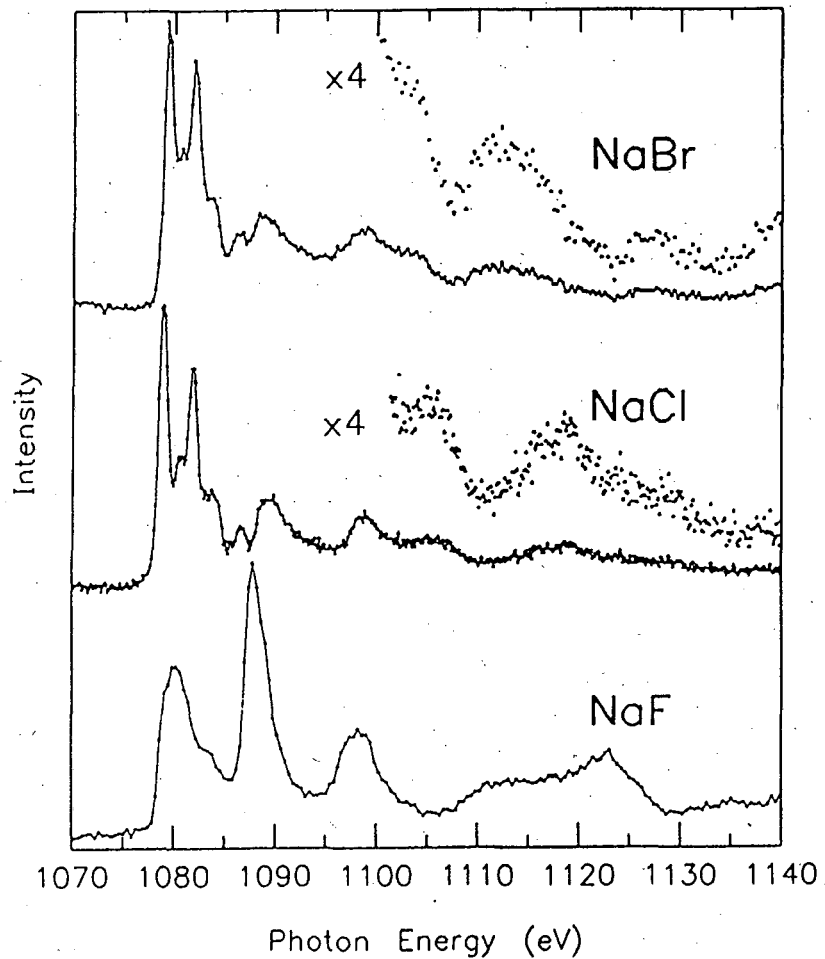


Figure 1: Photoabsorption spectra of sodium halide salts near the sodium K-edge. Some weaker absorption features are also shown with an expanded vertical scale.

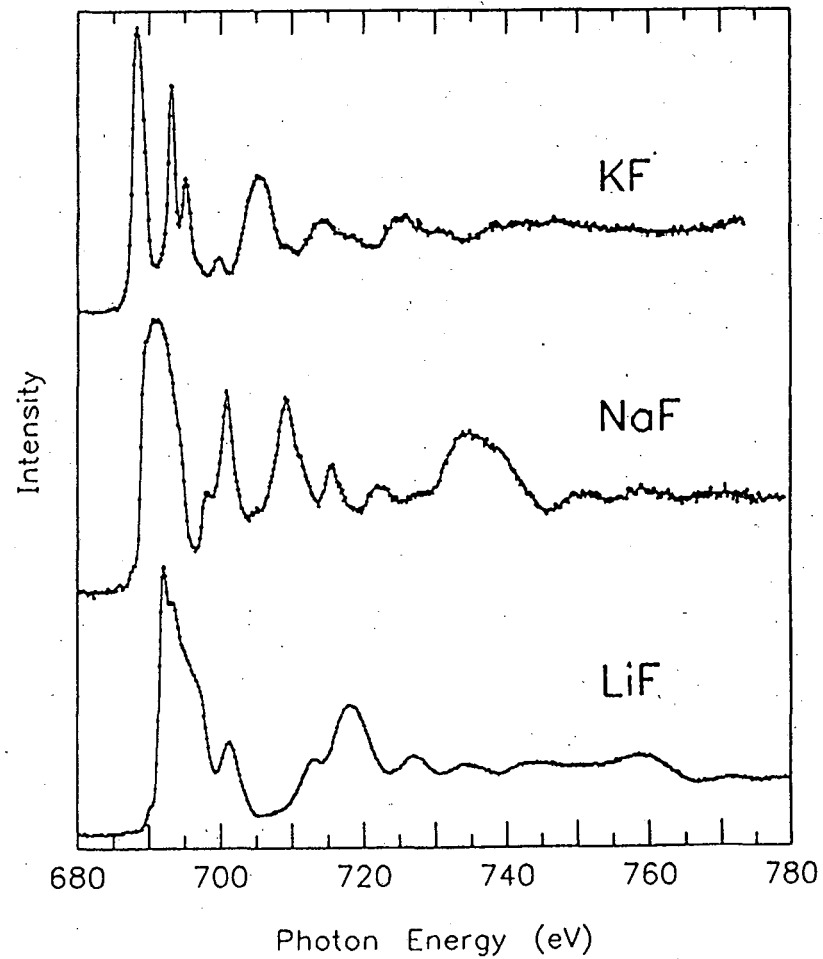


Figure 2: Photoabsorption spectra of alkali fluoride salts near the fluorine K-edge.

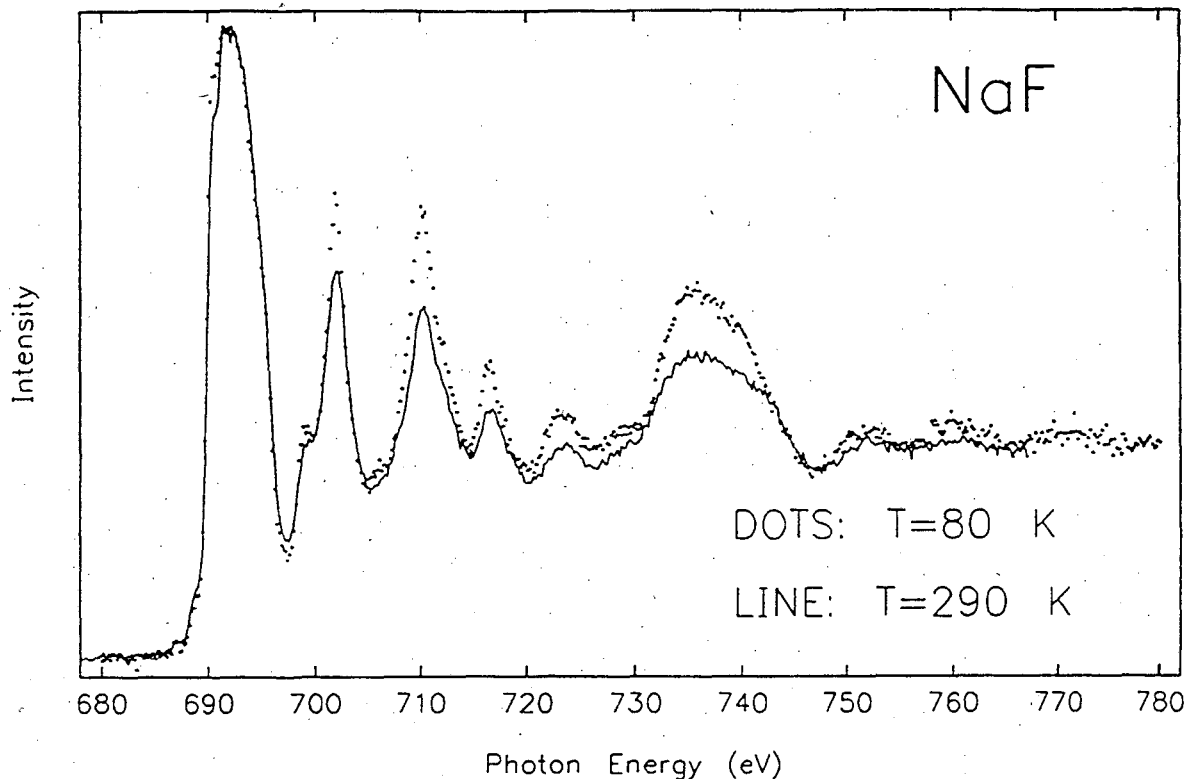


Figure 3: Temperature dependence of the NaF spectrum near the fluorine K-edge. At room temperature, the peaks are broader and less intense, with the exception of the lowest-energy feature.

temperature [5].

Spectra were also measured at room temperature for all the Na-K edges and for the F-K edge of NaF. In each case spectral features were broadened as compared to the low-temperature spectra. The temperature dependence of the F-K edge spectrum of NaF is shown in Fig. 3. Peaks in the room-temperature spectrum are distinctly weaker and broader, with the exception of the feature at 692 eV. For spectra at the Na-K edge of NaF and NaBr and at the F-K edge of NaF, the relative orientation of the x-ray linear-polarization vector and the crystal axes were varied. Spectra obtained with the polarization vector aligned along the [100], [110], and [111] crystallographic directions were virtually identical. The spectra shown in the figures here were all obtained with the [110] axis parallel to the x-ray polarization.

DISCUSSION AND SIMULATIONS

All of the spectra in Figs. 1 and 2 show sharp absorption features near threshold and broader resonances extending 60-90 eV above threshold. The narrow lines below and just above threshold are attributed to core-level excitons, i.e. the excitation of the core electron into a bound or quasi-bound state just below the conduction band. The broader peaks above threshold are assigned to photoelectron multiple-scattering resonances. These prominent features are observed when a single electron is promoted to an unbound state which is resonantly enhanced at the absorber by multiple scattering from the surrounding ions. This is not a sharp distinction; In both cases the presence of the core hole has a strong influence on the final states [6] and multiple scattering can be used to model the final states [5,7].

In general, multi-electron excitations may also produce fine structure above absorption edges. Such features are the result of the simultaneous promotion of a core electron and one or more valence electrons to a bound final state. These excitations are observed in many systems but are generally much less intense than the features observed here. For comparison purposes, the K-edge spectrum of Ne gas was measured with high resolution using the SX700/II monochromator at BESSY [8]. Atomic Ne is isoelectronic to Na^+ and F^- ions. Fig. 4 shows the K-edge spectra for Ne gas and for sodium and fluorine in NaF, aligned at the lowest-energy inflection points.

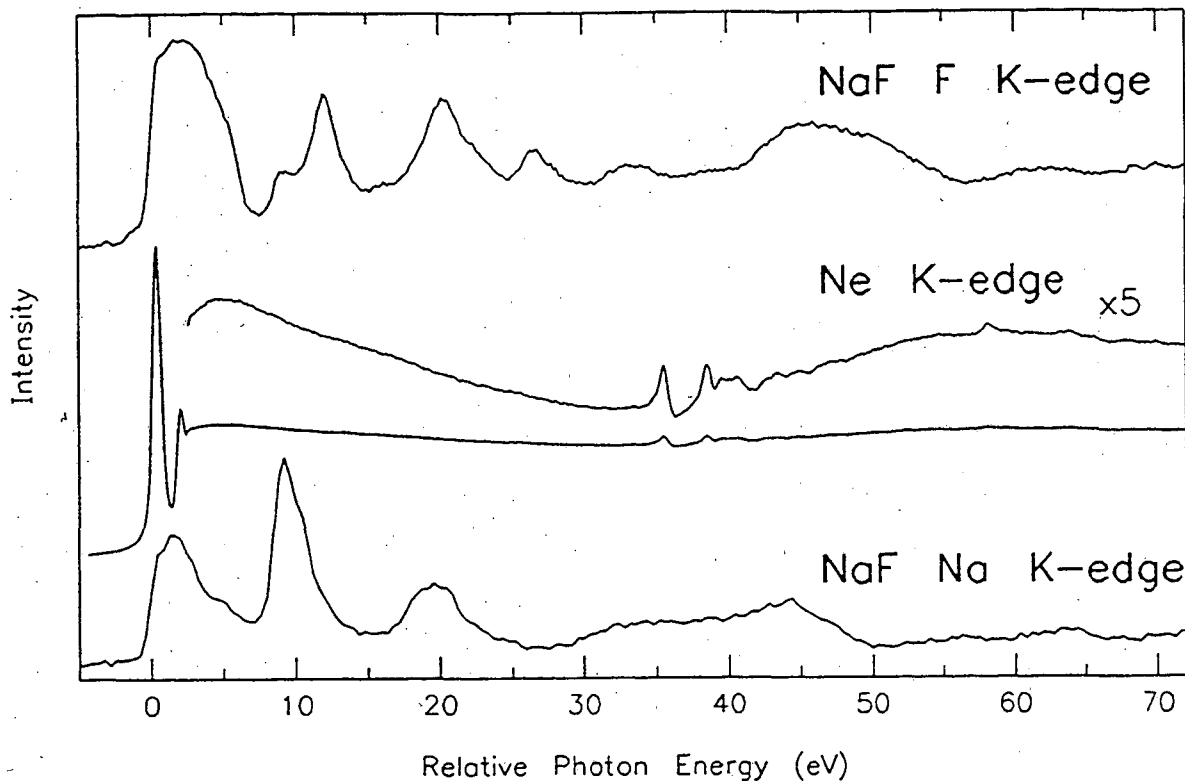


Figure 4: Comparison of the K-edge spectra of sodium and fluorine in NaF with that of neon gas. The above-edge structure in the Ne spectrum, also shown with an expanded vertical scale, arises from multi-electron excitations.

The Ne spectrum shows weak, narrow peaks at $\approx 35-45$ eV and 58 eV which are attributed to multi-electron excitations (scattering resonances are not possible for a lone atom). However the combined intensity of these features is only a tiny fraction of the total area under the step function for this absorption edge. This result strongly suggests that contributions of multi-electron excitations will be very weak in the alkali halide XANES spectra presented here.

Further support for the assignment of the above-edge absorption structure to single-electron scattering resonances is provided by the observed temperature dependence of the spectra (e.g. Fig. 3). In comparison, the features of the lower-temperature spectra are sharper and more intense. These differences indicate the dependence of the resonances upon the positions of the ions in the lattice. At higher temperatures, the larger variation in the local lattice structure broadens the absorption features. This effect is expected to be much larger for one-electron multiple-scattering resonances than for multi-electron excitations. In Fig. 3 the lowest-energy peak, at 692 eV, shows very little temperature dependence. This result suggests that the associated excitonic state arises primarily from electron-hole interactions rather than the effect of the potential barrier produced by the neighboring ions (i.e. a scattering resonance).

As mentioned above, some spectra were measured with different orientations of the x-ray polarization vector with respect to the crystal lattice. Surprisingly, the spectral features showed no dependence upon this change in experimental geometry. Such a dependence was expected, in particular, for the features closest to the absorption edge because of the well-defined spatial symmetries of similar XANES resonances in free and adsorbed molecules [9]. The lack of a polarization effect suggests that the excited states observed in the individual spectra share the same spatial symmetry.

The *ab-initio* curved-wave electron scattering code FEFF developed by Rehr and coworkers allows the calculation of Extended X-ray Absorption Fine Structure (EXAFS) spectra [1]. A recently released version (FEFF V) also calculates contributions from multiple-scattering paths, which are important at lower electron energies [2]. This version is therefore appropriate for the modeling of XANES spectra at energies above threshold. Preliminary calculations using FEFF V have been performed for all spectra presented here. The characteristics of alkali halide crystals are

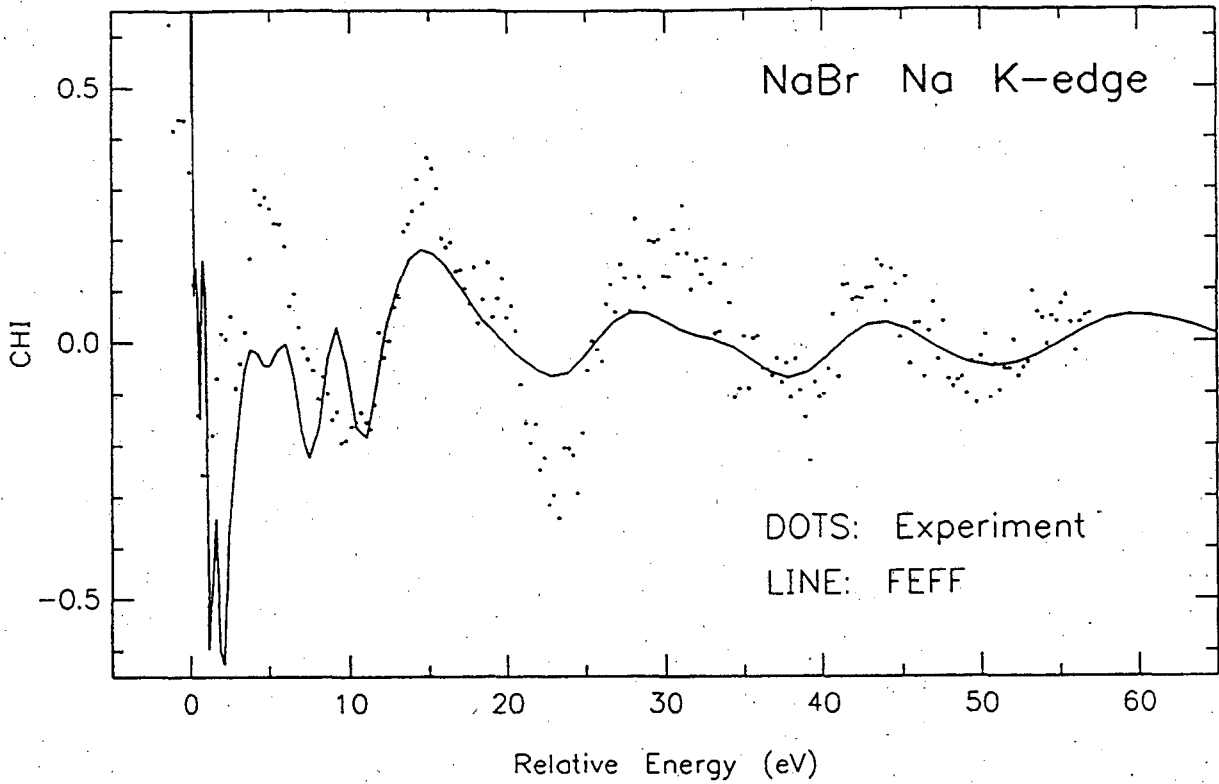


Figure 5: Comparison of experimental (dots) and theoretical (line) $\chi(E)$ for the sodium K-edge of NaBr. Agreement is best above ≈ 10 eV.

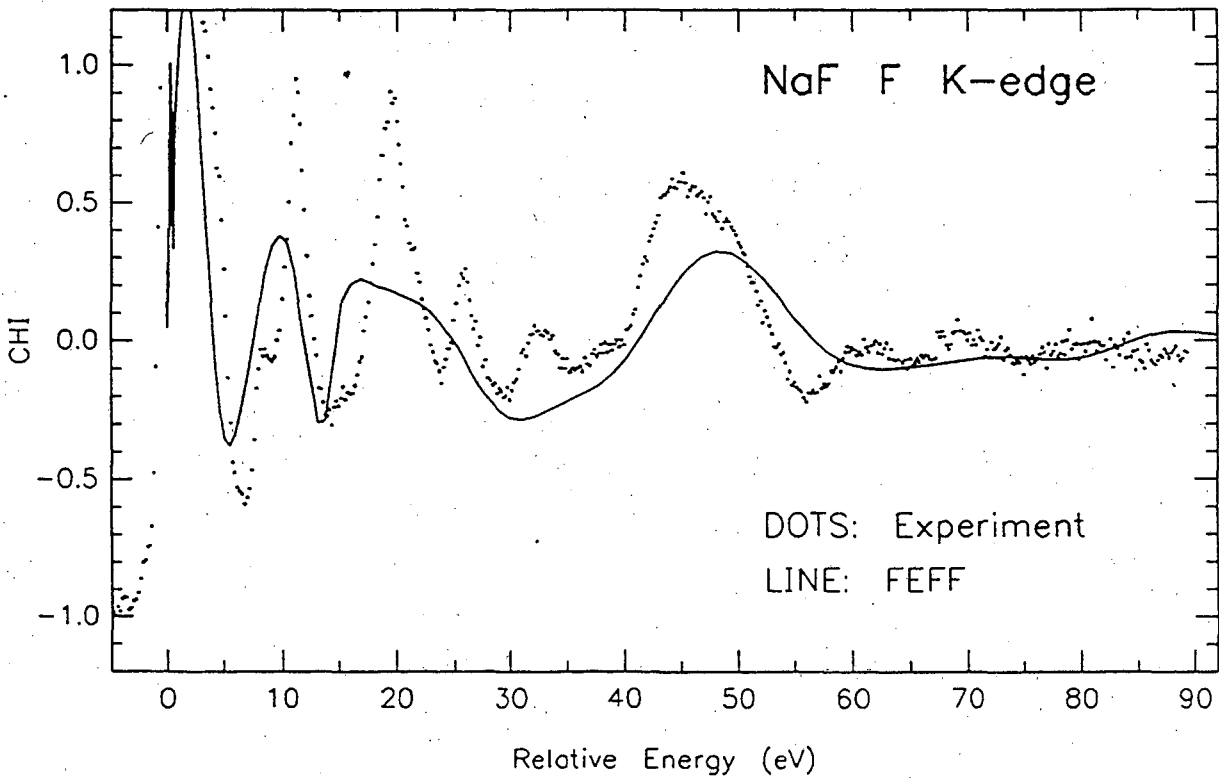


Figure 6: Comparison of experimental (dots) and theoretical (line) $\chi(E)$ for the fluorine K-edge of NaF. The lower-frequency oscillations are modeled better than the higher-frequency features.

well-known, and therefore no adjustable parameters were used for the simulation, besides the energy of the ionization threshold. Lattice constants were taken from Ref. 10 and Debye temperatures from Ref. 11.

The preliminary simulation results from FEFF ranged from good to fair agreement with experiment. In several cases, the amplitudes in the simulations were much less than in the experimental spectra. In FEFF, the amplitude scaling factor is essentially an adjustable parameter, but normally is closer to unity [1]. The spectral regions 0-10 eV above threshold were not well-modeled in some spectra, even using very large clusters (515 atoms; 26 shells). Higher energy ranges were more successfully modeled, e. g. for the sodium K-edge of NaBr, as shown in Fig. 5. Overall, the fluorine K-edge spectra were not predicted as well as the sodium K-edge spectra. Fig. 6 shows the results for the fluorine K-edge of NaF, where mainly the broader oscillations of the data are reproduced by the calculation. The present results indicate at least partial success for FEFF in the prediction of alkali halide XANES spectra.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720