PHYSICAL REVIEW B VOLUME 21, NUMBER 10 15 MAY 1980

Temperature dependence of the soft x-ray emission edges of simple metals

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(Received 19 November 1979)

The widths and energy positions of the $M_{2,3}$-emission edge of potassium, K-emission edge of beryllium, and $L_{2,3}$-emission edges of aluminum and magnesium have been measured for temperatures between 80 and 600 °K. All band edges broaden ($\Delta\Gamma$) and shift in energy (ΔE) with increasing temperatures for these materials. Similar results were reported earlier for the Li K-emission edge and Na $L_{2,3}$ edge. Lattice-relaxation processes and the phonon core-hole interaction are the dominant mechanisms affecting the core-level widths and the experimentally observed edge widths. The edge shifts are found to be proportional to the thermal expansion of the lattice, and are discussed in terms of the electron energy-level shifts which occur as the lattice dilates.

I. INTRODUCTION

Over the years a great effort has been made by many workers to understand the physical processes affecting the shape of the soft x-ray emission edges in metals.[1–7] Recently much attention has been paid to the broadening processes affecting the core levels and the experimentally observed edge widths.[5,6,8–11] At finite temperatures the lattice vibrates with the result that the localized core electrons are imbedded in a changing Coulomb potential. The theory of this effect predicts a broadening of the emission and absorption edges due to the electron-phonon or core-hole-phonon interaction.[8–10] With increasing temperature, the lattice expands so that there is less overlap of the screened ionic potential, a reduction of electronic density, and a change in the screening. These effects change both the edge broadening and energy position. The temperature dependence of the electronic band structures has been calculated[12] for a few metals [e.g., Cu, Ca (Ref. 12)] and the general theory has been described.[13] However, core-level binding-energy shifts have not been calculated as a function of the temperature for most metals.[14]

Information about the effects described above may be obtained from measurements of the temperature dependence of the soft x-ray edges of simple metals. In this paper, we report new measurements of the edge widths and positions as functions of temperature for the Be K spectrum, the K $M_{2,3}$ spectrum, and the Al and Mg $L_{2,3}$ spectra. The results are analyzed along with similar results previously reported for the Li K spectra[15] and Na $L_{2,3}$ spectra.[16]

The emission spectra were measured for temperatures ranging from 80 °K up to the melting points of Li, Na, and K and to about 600 °K for Be, Mg, and Al. Edge widths and positions were determined from the spectral data by methods described in detail elsewhere.[15–17] Edge widths are determined primarily by the thermal broadening of the core level. The observed values are in generally good agreement with a recent theoretical calculation of the phonon-core-hole interaction.[9,11]

Much less theoretical attention has been paid to the effects of temperature on the energy position of the x-ray edge. Our basic results are that the edge shifts are proportional to the lattice dilation, that with increasing temperature, the shifts are towards higher photon energies for Li, Na, and K, and are to lower energies for Mg, Al, and perhaps Be. We find that simple models which treat the core levels and conduction-band states independently are not capable of explaining these observations, because the relative energies of the core and Fermi levels determines the energy of the x-ray edge. Tagle and Stocks, using the Korringa-Kohn-Rostoker (KKR) band-theory method, have calculated the effects of lattice dilation on both the core level and conduction-band states for K and Al.[18] They find that both core level and conduction band shift to higher energies as the lattice dilates, but that the greater shift of the conduction-band states results in a net increase of the energy separation between the core level and Fermi level. The resulting predicted increase in the energy of the x-ray edge is in qualitative agreement with experimental results for K but not for Al, where the observed shift is to lower energy.

II. EXPERIMENTAL PROCEDURES

Most of the equipment used has been described elsewhere.[15,16] Here we describe briefly the experimental procedures used in making the measurements reported in this paper. All the metals were evaporated in situ onto a Cu anode, which was cooled by circulating coolant (liquid nitrogen, dry-ice-methanol mixture, ice water, and compressed air). In the case of the Al and Mg edge measurements, three different temperatures were used (liquid nitrogen, tap water, and ~600 °K). The 600 °K was obtained by allowing the Cu anode to increase in temperature from the electron beam heating. The temperature was monitored by a thermocouple clamped to the emitting surface.

An 8- to 10-mA beam of 1.9- to 2.2-keV electrons was incident at 45° to the anode surface. Due to the low melting point of K, this electron beam easily melted the sample when no cooling was present. It was necessary to cool the sample carefully by regulating compressed air circulation to obtain the K data at 317 and 339 °K. The UHV chamber base pressure rose from 2×10^{-9} to 8×10^{-9} Torr when it was connected with the grazing-incidence monochromator. The pressure rose again to 2×10^{-7} Torr during the evaporation and dropped to 3×10^{-8} Torr when the evaporation was stopped. A Ti sublimation pump baffle was cooled with liquid nitrogen during the experiments to increase the speed of pumping H_2O and other contaminants.

The emitted photons were measured using a 2.2-m grazing-incidence monochromator fitted with a channeltron detector. Two different diffraction gratings were used for the different energy ranges of the spectra measured. An Al-coated 300 l/mm grating was used to record the $M_{2,3}$-emission edge of K, and a 1200 l/mm gold-coated grating was used to record the other spectra. Spectra generated by a condensed spark discharge in air were used to calibrate the monochromator. Fifteen or twenty separate measurements of each spectra were averaged to raise the signal-to-noise ratio of the high-resolution ($\simeq 0.1$ eV) measurements. Spectral data were digitized at 0.015- to 0.030-eV intervals, depending on the energy ranges. All the data are arbitrarily scaled after dividing the yield intensity by E^5, where E is the photon energy. The E^5 compensates for frequency factors appearing in the dipole matrix elements (E^3) and for the changing energy resolution of the monochromator (E^2) so that the spectra can be more directly compared with calculated densities of states.

III. EXPERIMENTAL RESULTS

Our interest in this paper is in the energy position and width of the Fermi edge of the x-ray spectra. Some care must be used in determining these parameters from the data in cases where many-body and/or band-structure effects give structure in the spectral density at the Fermi edge. For Al, Mg, and K, edge positions and widths were determined by folding a Gaussian broadening function with a one-electron-transition edge spectrum that was modified by a many-body peaking parameter at the Fermi edge, using the procedures previously described for Na.[16] Good fits to the spectra were obtained using a square-edged one-electron spectrum for all cases except Mg where a narrow-band-structure peak at the band edge had to be assumed in order to fit the data.[19] The K-emission edge of Be was fitted using a one-electron spectrum folded with a Gaussian broadening function following the procedure previously used for Li.[15] No evidence for many-body peaking effects are observed for Be. The detailed results of the analysis of the edge for band-structure and many-body effects will be the subject of a separate paper.[17]

The $M_{2,3}$-emission edge spectra of K at 93, 223, 284, 317, and 339 °K are presented in Fig. 1. The spectra were taken with 150-μm slit widths using the 300 l/mm Al-coated diffraction grating. An instrumental resolution of 0.064 ± 0.016 eV was measured from the half-width of single lines in the spark spectrum. These curves show a broadening and an energy edge position shift to higher energies as the temperature is increased. A Gaussian function with full width at half maximum (FWHM) of 0.064 eV was used to remove part of the edge broadening due to the instrumental response function. For determining changes with temperature we assume that the edge is symmetrically broadened.[16]

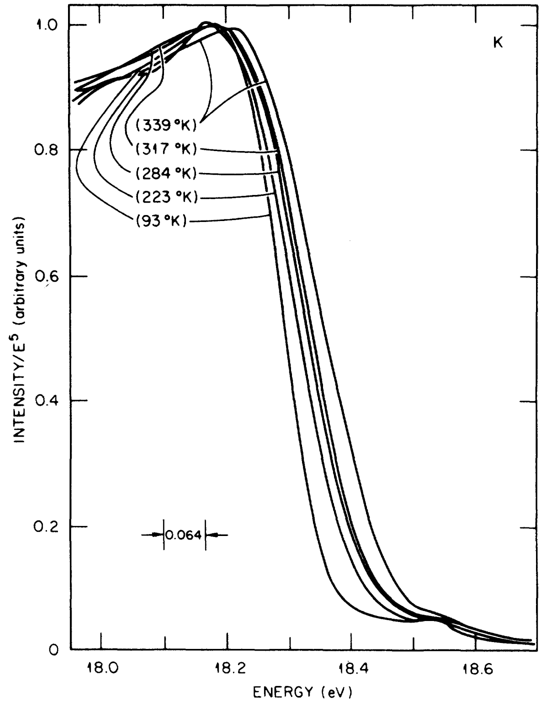

FIG. 1. Soft x-ray $M_{2,3}$-emission edge for K between 93 °K and above the melting point.

TABLE I. Emission-edge position at room temperature (E), the edge shifts (ΔE), and linear expansion ($\Delta L/L$) observed for temperature changes (ΔT). Values of ΔE are taken from Figs. 1 and 3–5, and from Refs. 15 and 16. Values of $\Delta L/L$ are taken from Refs. 21 and 22.

	$E(T=300\,^\circ\mathrm{K})$ (eV)	ΔT(°K)	ΔE(eV)	$\Delta L/L$(%)
Be	112.00 ±0.10	340 ± 5	≃ 0.00 ± 0.0	0.259 ± 0.02
Mg	49.470 ± 0.026	356 ± 5	−0.021 ± 0.005	0.844 ± 0.03
AL	72.636 ± 0.036	530 ± 5	−0.076 ± 0.010	1.232 ± 0.04
Li	54.830 ± 0.020	405 ± 5	0.100 ± 0.020	1.559 ± 0.06
Na	30.576 ± 0.025	295 ± 5	0.085 ± 0.020	1.667 ± 0.05
K	18.307 ± 0.010	246 ± 5	0.066 ± 0.020	1.485 ± 0.02

The edge energy positions and widths are plotted in Fig. 2 as a function of temperature. The edge width increases approximately linearly with temperature with an additional increase upon melting. The photon energy of the edge increases nearly linearly with temperature. The slope ($\simeq 2.2\times10^{-4}$ eV/°K) can be compared with the earlier results reported for Li (Ref. 15) ($\simeq 1.5\times10^{-4}$ eV/°K) between 100 and 300 °K. A discontinuous shift of 0.032 ± 0.010 eV is also observed as the melting point is reached. These values and the results for the other metals are summarized in Table I.

In Fig. 3 the $L_{2,3}$-emission edge of Mg is presented for three different temperatures. A 1200 l/mm Au-coated diffraction grating was used with 75-μm slit widths to obtain a resolution of 0.078 ± 0.020 eV. The edge width increases with temperature, and a small shift of the edge to lower energies occurs. This shift is in the opposite direction to that observed for the alkali metals. The edge energy shift detected was very small ($\simeq$0.021 ± 0.005 eV), and we could not attain higher temperatures due to the fact that Mg sublimes at 449 °K for a base pressure of 10^{-8} Torr. This shift to lower energies is more pronounced for the Al $L_{2,3}$-emission edge which was measured at a higher temperature (623 °K). The Al spectra are shown in Fig. 4 and were taken using 50-μm slits and a resolution 0.143 ± 0.030 eV on the spectrometer. The Al edge also broadens with increasing temperature.

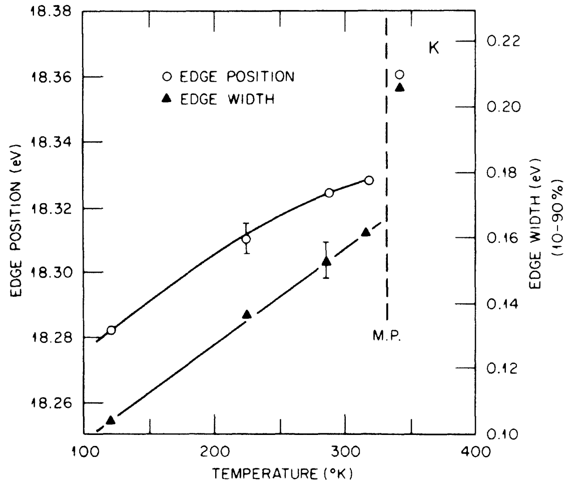

FIG. 2. Temperature dependence of the edge width and edge position for the $M_{2,3}$-emission spectra of K.

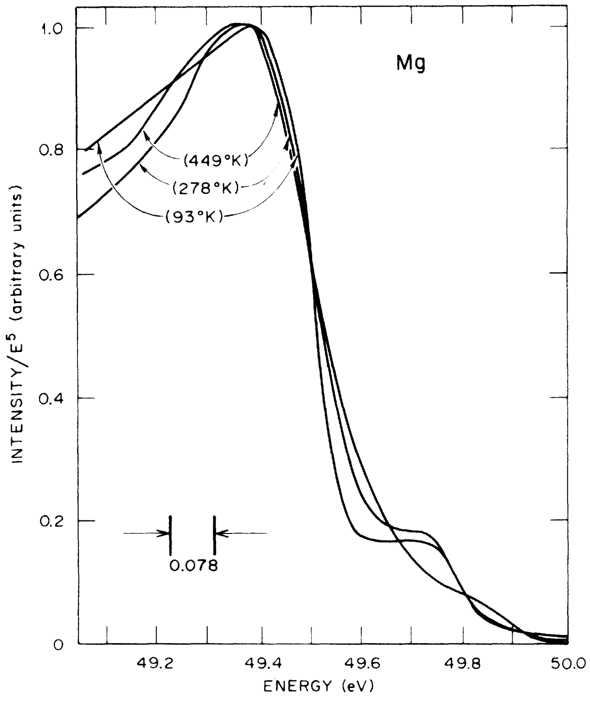

FIG. 3. $L_{2,3}$-emission edge for Mg between 93 °K and the sublimation temperature (449 °K) at 2×10^{-8} Torr base pressure.

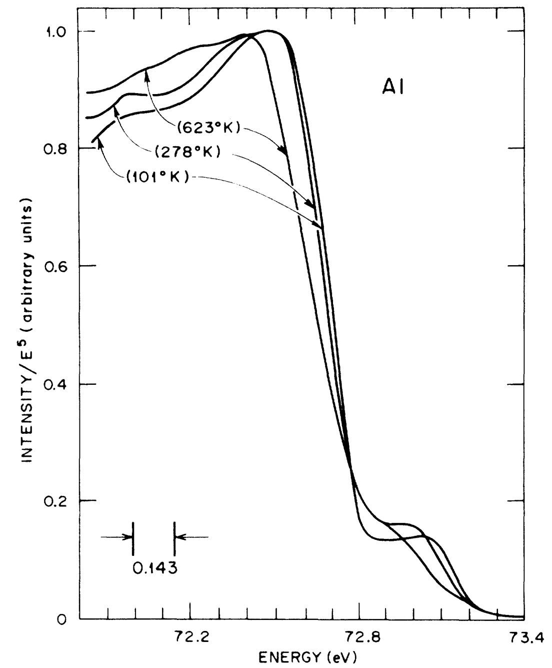

FIG. 4. $L_{2,3}$-emission edge for Al between liquid-nitrogen temperature (101 °K) and 623 °K.

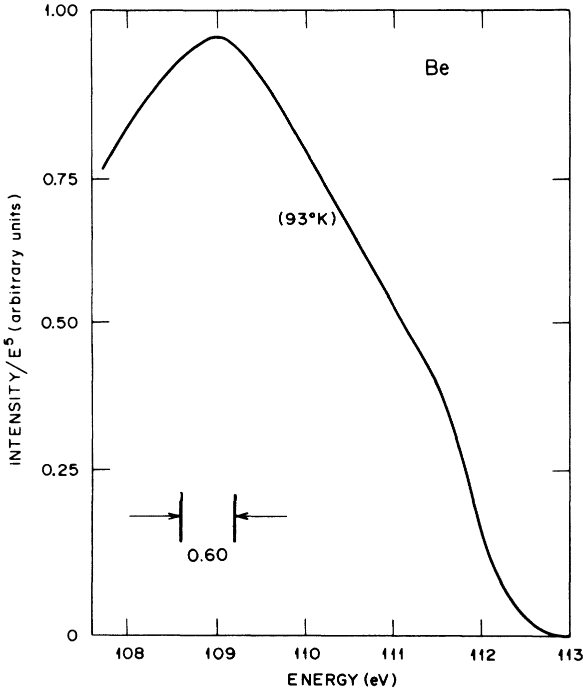

FIG. 5. Be K-emission edge of 93 °K.

We report in Fig. 5 the shape of the Be K-emission edge. The low intensity for the emission spectrum of Be necessitated the use of wider slits (150 μm) which gave a resolution of 0.60 ±0.05 eV. We measured the Be edge for five different temperatures, but no shifts or temperature broadening was observed within the resolution of our measurements. However, recent self-absorption measurements of Crisp[20] show a temperature shift of the Be edge of $\sim +0.1$ eV between 80 and 340 °K, using an instrument resolution of 0.26 eV in the fourth order.

IV. DISCUSSION

A comparison of the x-ray edge shifts with the thermal expansion coefficients as a function of temperature makes it clear that the main source of the edge shift is the thermal dilation of the lattice. Because of the experimental uncertainties in the edge position measurements, however, we cannot demonstrate that the edge shift has exactly the same dependence on temperature as the linear expansion coefficient. Nevertheless, in the following discussion, we assume that the edge shift results solely from the change in lattice constant and do not consider other mechanisms.

In addition to confirming that the edge shift in any given metal is approximately proportional to the expansion coefficient, we looked for empirical relationships common to all the materials. A potentially interesting result is shown in Fig. 6 where $(\Delta E/E)/\Delta T$ is plotted versus $(\Delta l/l)/\Delta T$. Here ΔE is the edge shift and Δl the linear expansion occurring as the temperature is increased from 100 to 300 °K, and E is the edge energy. Values of $\Delta l/l$ have been taken from Refs. 21 and 22. A monotonically increasing dependence is found for the alkali metals Li, Na, and K. No such regularity is found when $\Delta E/\Delta T$ is plotted versus the expansion coefficient. Apparently the magnitude of the edge shift scales with the depth of the core level.

The experimental observations of the effective temperature on the emission edges show two primary features: the changing width and the edge shifts. We will discuss the edge shapes in terms of a phonon-core-hole interaction. We will not discuss the effects of band structure, conduction electron-core-hole interactions, or final-state interactions (many-body effects) all of which may affect the shape. These have been discussed theoretically by Almbladh, Hedin, and Mahan and will be the subject of a forthcoming publication.[17]

Almbladh and Hedin[9,10] have shown that the thermal broadening of the core level due to the phonon-core-hole interaction of $\simeq 10$ kT $\simeq 0.1$ eV is the dominant mechanism responsible for the experimentally observed edge widths. The thermal broadening at the Fermi edge ($\simeq$kT $\simeq 0.01$ eV) and the core-

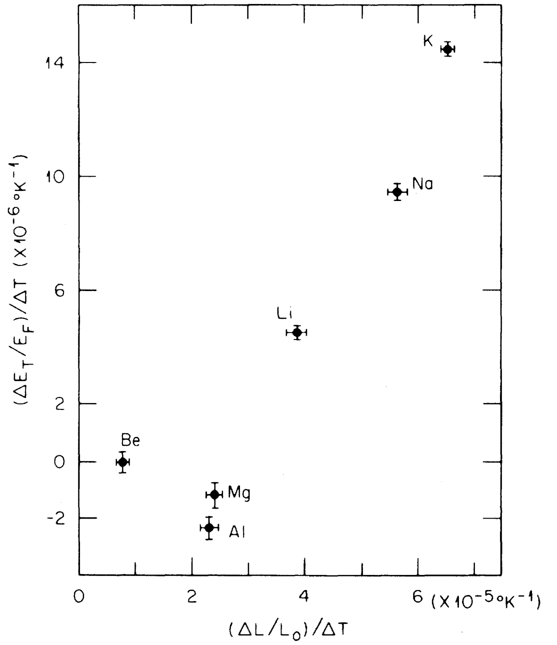

FIG. 6. Dependence of energy edge position on the linear thermal expansion coefficients for different metals.

hole lifetime ($\simeq 0.01$ eV) are very much smaller. According to the phonon-core-hole interaction theory recently developed,[9,11] if the lifetime of the core hole is comparable to the lattice-relaxation time, the lattice has time to partially relax before emission takes place. The incomplete relaxation theory of Almbladh and Mahan has been reviewed recently by Hedin.[6] Partial relaxation effects are apparently responsible for the anomalous shape of the Li emission edge and may account for the fact that the emission edges of Na and K are less peaked than the absorption edges.

On the other hand, no theoretical discussion of the shift of the core levels with temperature has appeared in the literature. The energy shifts occur in both emission and absorption spectra. They can be attributed to small changes in the electronic energy levels as the lattice expands with increasing temperature.

Some of these shifts can be estimated using simple models. In a free-electron metal, lattice dilation results in a reduction in electron density and a lowering of the Fermi level with respect to the bottom of the conduction band. More realistic models give the same qualitative result; the conduction band narrows as the lattice dilates. As for the core levels, since they occupy compact orbits near the center of the Wigner-Seitz cell, their shifts may be viewed as resulting from the change of potential near the center of the cell as adjacent atoms move away. Assuming that nearest-neighbor ion cores contribute a Thomas-Fermi screened potential at the central atom,[23] with screening length dependent on electron density, a simple calculation leads to the result that the core levels move upward in energy as the lattice expands.

These qualitative results on conduction-band narrowing and the direction of the core-level shifts are not likely to be in error for reasonable crystalline potentials. Combined with the assumption of a fixed energy separation between core and conduction-band levels, they would result in a reduction of the core-level—Fermi-level separation and a shift in the x-ray edge to lower energies as the lattice dilates. Our observations of shifts to higher energies in the alkali metals Li, Na, and K lead us to conclude that, as the lattice dilates, the conduction band shifts upward in energy more rapidly than the core levels.

Precisely this result has been obtained by Tagle and Stocks in calculations of the core-level and conduction-band states of K using a KKR calculation.[18] In Fig. 7, the results are shown along the Δ direction for lattice spacings appropriate to temperatures of 93 and 340 °K.[21,22] The conduction band narrows and the core levels shift upward as is expected, but these effects are more than compensated by the shift of the conduction-band states to higher energies. A net increase in core level to Fermi-level spacing of +178 meV is obtained which may be compared with the experimentally observed shift of +70 meV.

In a similar calculation for Al, an increase in core-level to Fermi-level spacing of +75 meV was obtained from calculations appropriate to 110 and 660 °K. This may be compared with the observed negative shift of the x-ray edge of about −80 meV.

Though the calculations and observations do not agree in detail, they do seem to indicate that the observed shifts can find a reasonable explanation in

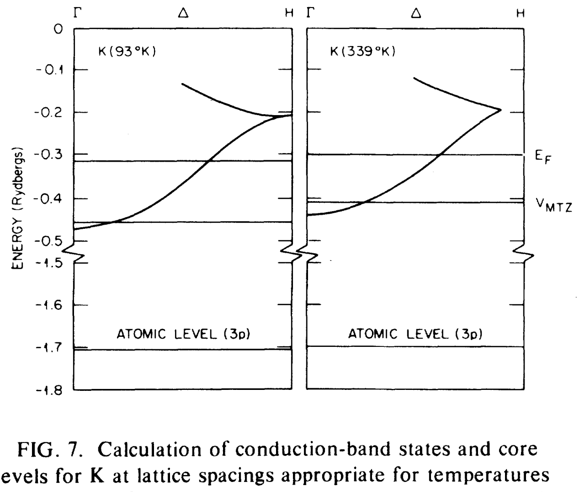

FIG. 7. Calculation of conduction-band states and core levels for K at lattice spacings appropriate for temperatures of 93 and 340 °K. V_{MTZ} is the muffin-tin zero potential, E_F is the Fermi level position. $\Delta E = (E_F - E_{3p})_{399\,°K} - (E_F - E_{3p})_{93\,°K} = 178$ meV is the calculated shift of the emission edge. Calculations are from Ref. 18.

terms of the effect of lattice expansion on the energies of core and conduction-band states. Moreover they suggest that the observed shifts can provide a very sensitive test of some features of the potentials used in band-structure calculations.

One additional physical process affecting the core-level position needs to be considered. Conduction electrons not only screen the potentials of the ion cores surrounding each atom but also screen the core hole that exists on the atom before the emission process takes place. If it is assumed that the emitting transition is to an energy level associated with a fully screened core state, then the change in screening associated with lattice dilation can significantly shift the core level downward in energy, as suggested by Citrin, Wertheim, and Baer.[24]

It is not clear, however, that such a calculation is appropriate. Von Barth and Grossman have shown that static screening for the core hole should produce a prominent low-energy peak in the *s*-like DOS of the simple metals, but this peak is not observed in the *L* spectra of Na, Mg, and Al.[25] They are able to account for this result by applying many-body theory and conclude that, short of performing a full many-body calculation, the emission spectra may be most appropriately calculated using the final-state potentials of the system. In our case, the core level is filled in the final state, and the appropriate calculations would be simply those of ordinary band theory.

If the final-state rule proves correct, the neglect of core-hole screening effects may be justified. In any case, additional theoretical work is needed to ascertain its effects on the energy shifts of core levels with temperature.

ACKNOWLEDGMENTS

This research was sponsored by the Office of Health and Environmental Research, U. S. Department of Energy, under Contract No. W-7405-eng-26 with the Union Carbide Corporation.

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