

## Experimental interatomic Auger rates in sodium halides

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Interatomic Auger transition rates of holes in the two outermost alkali-metal ion core levels have been measured in the sodium halides. The Na  $2s$  core hole, which decays via a singly interatomic Coster-Kronig process, has a lifetime width of  $0.75 \pm 0.15$ ,  $0.45 \pm 0.10$ , and  $0.46 \pm 0.10$  eV in NaF, NaCl, and NaBr, respectively. The  $2p$  hole, which decays via a doubly interatomic process, has a lifetime width of  $0.10 \pm 0.05$  and  $< 0.06$  eV in NaF and NaCl, respectively. The large phonon broadenings determined here, ranging from 0.7 to 1.0 eV in the different sodium halides, are in excellent agreement with calculated values and are responsible for the large uncertainty limits on the determined lifetimes. The absolute values of the Na  $2s$  and  $2p$  lifetime widths are comparable to those from theoretical calculations.

### I. INTRODUCTION

Because charge is transferred from metal to ligand valence states in the formation of an ionic compound, the shallowest cation core-hole states in many ionic materials should decay mainly by interatomic Auger processes involving anion valence electrons.<sup>1</sup> The existence of these processes was convincingly demonstrated by identifying the Auger electrons resulting from these transitions.<sup>2,3</sup> The corresponding interatomic Auger transition rates have been calculated for a number of systems,<sup>4-6</sup> but they have not been measured until now, to our knowledge, because of complications in the analysis due to large phonon broadening of the photopeaks<sup>7,8</sup> and the predicted<sup>9</sup> contributions of surface components in the data. Recently, and despite the dominant phonon broadening, we have confirmed the existence of such surface-ion core-level shifts in the halides of K, Rb, and Cs.<sup>10</sup> However, the binding energies of the alkali core and halide valence electrons<sup>10</sup> and the estimated two-hole correlation energies for the valence bands<sup>3</sup> in these systems indicate that the interatomic Auger process for the outermost  $p$  shell will be energetically forbidden. Only in the Na salts will the interatomic Auger process be clearly allowed by virtue of the larger Na  $2p$  binding energy.

Here, we present data for NaF, NaCl, and NaBr in which the Na  $2s$  hole state decays by a singly interatomic process and the Na  $2p$  hole by a doubly interatomic one. Results are also presented for RbBr data taken with He resonance radiation, which were reported in a study of the surface-ion core-level shift.<sup>10</sup> Comparisons are made with theoretical calculations for the Na  $2s$  core-hole lifetime width in NaCl,<sup>5</sup> and the  $2s$  and  $2p$  widths in NaF.<sup>6</sup> Finally, possible implications are discussed of interatomic Auger transitions in the recently determined large lifetime widths of outermost  $p$  states in alkali-metal atoms adsorbed on transition-metal substrates.<sup>11,12</sup>

### II. EXPERIMENTAL PROCEDURE

The experiments were carried out using films of alkali halides evaporated from carbon crucibles onto Si(111) or

Si(100) substrates in a preparation chamber attached to the photoelectron spectrometer. The photoemission measurements were made with synchrotron radiation using the Bell Laboratories—Brookhaven 6-m toroidal grating monochromator beam line at the National Synchrotron Light Source. Kinetic energies are reference to the vacuum level of the spectrometer, binding energies to the vacuum level of the sample. The latter was placed 21.22 eV above the low-energy cutoff in data taken with He I resonance radiation. The resolution of the electron analyzer was 0.10 eV, resulting in a total instrumental resolution in the range from 0.12 to 0.15 eV, depending on photon energy. The photon flux is estimated to be in the range  $10^{12} - 10^{13}$  cm<sup>-2</sup> sec<sup>-1</sup>.

We found that NaCl and NaBr surfaces are rapidly destroyed by photon-stimulated desorption of the halogen. Changes became apparent after only 5 min of exposure to the photon beam. There is an initial broadening and shift of the spectrum to higher binding energy as  $F$  centers are produced, leading ultimately to the appearance of Na metal on the surface. In order to minimize this problem, data were taken only on fresh surfaces. In the case of NaCl, it was possible to maintain a stable surface by heating the sample to  $\sim 500$  K. Data for RbBr were obtained with 40.8-eV He II resonance radiation, as previously described.<sup>10</sup>

The core-level photoemission lines were analyzed with Voigt function line shapes. These are produced by the convolution of a Lorentzian, representing the core-hole lifetime width, and a Gaussian, representing the combination of the phonon width<sup>7,8</sup> and the instrumental broadening. The phonon width in these ionic insulators is generally so large that the instrumental resolution of 0.12–0.15 eV causes only a small increase in the Gaussian width. The Na  $2p$  spin-orbit splitting of 0.16 eV is so small compared to the phonon width that it is not resolved in the data. The  $p_{3/2}$  and  $p_{1/2}$  components of the Na  $2p$  doublet were consequently constrained to have the same line shape, a splitting of 0.16 eV, and a statistical intensity ratio of 2:1. The phonon widths were allowed to assume independent values for the bulk and the surface components.<sup>13,14</sup>

### III. RESULTS AND DISCUSSION

For a study of the interatomic Auger process, the most interesting data are those from the Na  $2s$  level in NaF and NaCl because in these systems the interatomic decay rates have been calculated to be large.<sup>5,6</sup> For a Na  $2s$  core hole, the Coster-Kronig process  $L_1L_{2,3}L_{2,3}$  is energetically forbidden; since the Na  $3s$ -derived conduction band in these ionic salts is essentially empty, there is also little contribution from the  $L_1L_{2,3}M_1$  process. Accordingly, a hole in the Na  $2s$  level predominantly decays via a singly interatomic Coster-Kronig process involving one electron from the Na  $2p$  level and one from the halogen-derived valence band, i.e.,  $L_1L_{2,3}(F)L_{2,3}$  and  $L_1L_{2,3}(Cl)M_{2,3}$ . The calculated Na  $2s$  widths are 0.64 eV for NaF (Ref. 6) and 0.79 eV for NaCl.<sup>5</sup> For comparison, in metallic Na where the intra-atomic  $L_1L_{2,3}M_1$  process does occur (since the Na  $3s$ -derived conduction band is half filled), the width is 0.28 eV.<sup>15</sup> The calculations thus indicate that for this level the interatomic process is faster than the intra-atomic one (see Table I).

Data for NaCl are shown in Fig. 1(a). A fit with a single peak shows that it is slightly asymmetric, as evidenced by the nonstatistical residuals. This suggests that there are distinct contributions from the bulk and the surface, as was found in previous work on the halides of K, Rb, and Cs.<sup>10</sup> The single-peak fit yields a lifetime width of 0.40 eV and a phonon width of 1.20 eV. The latter is much larger than that calculated from parameters given by Mahan,<sup>16</sup> indicating that there is more than one component in the data. Fits with two peaks using four independent width parameters do not converge to consistent values in different data sets. Consistency is, however, obtained by constraining the lifetime width of the surface component relative to that of the bulk. We have made the assumption that the interatomic decay rate depends linearly on the overlap with charge in the halide-derived valence band, so the surface lifetime width was constrained according to the number of Cl neighbors, i.e.,  $\frac{5}{6}$  of the bulk width for a singly interatomic process and  $\frac{25}{36}$  for a doubly interatomic one. [A surface Na

ion on the nonpolar (100) surface has five Cl neighbors, while a bulk Na ion has six.] It is important to note that the results quoted here are not sensitive to this particular assumption. For example, if we constrain the surface lifetime width to be simply equal to that of the bulk component, the only significant change is a small decrease in the surface phonon width.

Using the above approach in our analysis leads to the results shown in Fig. 1(b). The surface-ion core-level shift is  $0.48 \pm 0.03$  eV, close to the average shift of  $0.45 \pm 0.03$  eV measured for a variety of other alkali halides.<sup>10</sup> The lifetime width of the bulk component in this spectrum is 0.43 eV and the bulk phonon width 1.04 eV. The latter is in good agreement with the theoretical results of Mahan<sup>16</sup> for a temperature of 515 K. The surface phonon width is found to be 14% larger than the bulk width, a trend consistent with other results from metal systems.<sup>13,14</sup> The uncertainty in the present phonon widths is  $\pm 0.03$  eV, which was estimated from the reproducibility in the analysis of various independent data sets. The best value for the lifetime width, consistent with all sets of data, is  $0.45 \pm 0.10$  eV. The uncertainty here is determined mainly by the sizes and uncertainties in the phonon widths. Despite these relatively large errors and the fact that the lifetime width is significantly smaller than the calculated value of 0.79 eV,<sup>5</sup> we nevertheless do confirm the prediction<sup>5</sup> that the interatomic Auger rate for a Na  $2s$  hole in NaCl is faster than the corresponding intra-atomic process in Na metal.

The Na  $2p$  spectrum of NaCl at 450 K is shown in Fig. 2. The bulk and surface components include the unresolved spin-orbit splitting. The surface-ion core-level shift is  $0.47 \pm 0.02$  eV, in very good agreement with the value determined from the Na  $2s$  spectrum. A weak third component at larger binding energy is required to obtain a satisfactory fit. It arises from the modification of the surface by Cl desorption and is much stronger in data taken at room temperature. The absence of obvious Lorentzian tails makes it clear that there is very little lifetime broadening. A fit to the data yields a lifetime width of 0.04 eV. Since this value is small compared to the

TABLE I. Lifetime and phonon widths (in eV) of Na  $2s$  and  $2p$  levels in Na metal and Na halides.

	Lifetime width				Bulk phonon width	
	$\Gamma_{2s}$		$\Gamma_{2p}$		$\Gamma_{ph}$	
	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.
Na	$0.28 \pm 0.03^a$	$0.40^b$	$0.01^c$	$0.003^b$	$0.14 \pm 0.01^d$	$0.15^e$
NaF	$0.75 \pm 0.15$	$0.64^f$	$0.10 \pm 0.05$	$0.15^f$	$1.02 \pm 0.03$	$1.04^g$
NaCl	$0.45 \pm 0.10$	$0.79^h$	$< 0.06$		$1.03 \pm 0.02$	$1.02^g$
NaBr	$0.46 \pm 0.10$		$(0.04)^i$		$0.70 \pm 0.02$	

<sup>a</sup>Reference 15.

<sup>b</sup>T. Kobayashi and A. Morita, J. Phys. Soc. Jpn. **28**, 457 (1970).

<sup>c</sup>Reference 17.

<sup>d</sup>G. K. Wertheim, D. M. Riffe, and P. H. Citrin, Phys. Rev. B **49**, 2277 (1994).

<sup>e</sup>L. Hedin and A. Rosengren, J. Phys. F **7**, 1339 (1977).

<sup>f</sup>Reference 6.

<sup>g</sup>Calculated for NaF at 300 K and NaCl at 500 K from parameters in Ref. 16.

<sup>h</sup>Reference 5.

<sup>i</sup>Error limits could not be determined.

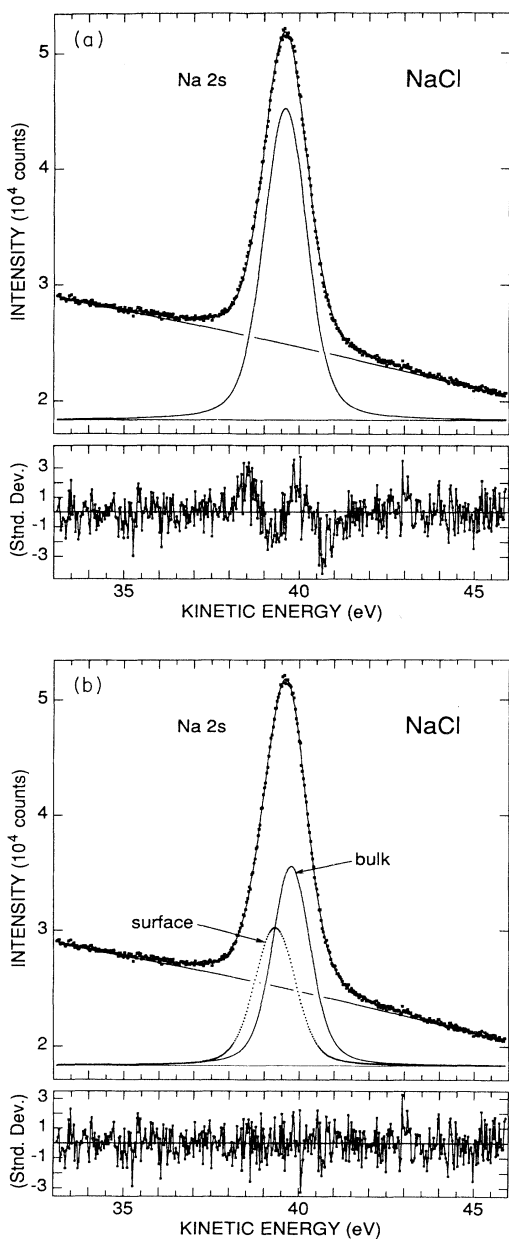


FIG. 1. (a) Na 2s photoemission spectrum of NaCl at 515 K, fitted with a single Voigt function. Note the systematic deviation in residuals. Data were taken with 110-eV radiation. (b) Same data as in (a), fitted with two Voigt functions representing bulk and surface contributions. Note the significant improvement in the residuals.

1.03-eV phonon width, it is inherently poorly defined by the data. Tests made by constraining the lifetime widths to a broad range of values show that satisfactory fits are obtained for  $0 < \Gamma_{2p} < 0.06$  eV. Although a definitive value cannot be obtained, we can say that the Na 2p hole-state lifetime in NaCl is not nearly as large as the theoretical value of 0.15 eV in NaF.<sup>6</sup>

In data for NaBr taken at 300 K, the Na 2s photopeak lies on the low-energy tail of the much stronger and rela-

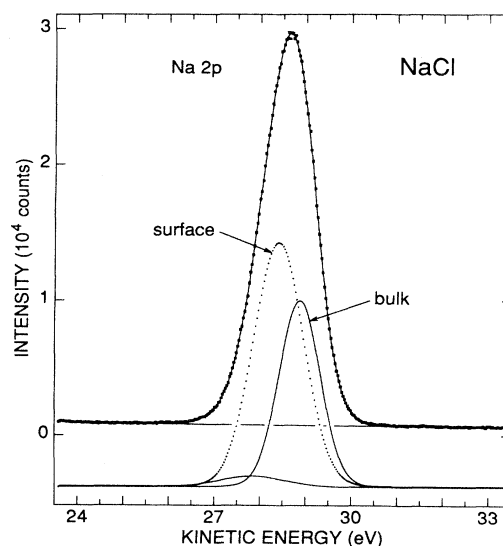


FIG. 2. Na 2p photoemission spectrum of NaCl at 450 K, fitted with bulk and surface components. Data were taken with 66-eV radiation. A weak component at the surface due to Cl photodesorption is also apparent.

tively broad Br 3d spectrum, producing a curved, sharply rising background. The data yield a Na 2s lifetime width of 0.46 eV, with an uncertainty estimated to be  $\pm 0.10$  eV. The Na 2p spectra have strong surface-related lines at larger binding energy, very much like the NaCl data, and yield a value for  $\Gamma_{2p}$  of 0.04 eV. These surface components prevent a more detailed investigation of limits on the 2p lifetime width. The phonon width is  $0.70 \pm 0.02$  eV, and the surface-ion core-level shift is  $0.49 \pm 0.02$  eV.

In the Na 2p data from NaF taken at 300 K, information about the bulk lifetime width is compromised by the overlapping F 2s line at lower binding energy and the surface component at higher binding energy; see Fig. 3. As a result, excellent fits can be obtained for lifetime widths in the range  $0 < \Gamma_{2p} < 0.20$  eV, with only modest changes in the phonon widths. The best fit yields a bulk phonon width of  $1.02 \pm 0.03$  eV, in very good agreement with the calculated phonon broadening of 1.04 eV obtained from data in Ref. 16. The surface-ion core-level shift is larger than in NaCl, and generally lies within the range of  $0.60 \pm 0.04$  eV. It is strongly anticorrelated with the surface phonon width, which is 10–20% larger than the bulk value. Although satisfactory fits are obtained with lifetime widths in a relatively large range, the extreme values can be ruled out because they result in bulk phonon widths far from those calculated.<sup>16</sup> The most reliable value for  $\Gamma_{2p}$  is  $0.10 \pm 0.05$  eV, in marginal agreement with the calculated value of 0.15 eV (Ref. 6) but not sufficiently well defined to provide a critical test of the theory. The mean 2p lifetime width in NaF is, however, certainly larger than that in Na metal,  $0.011 \pm 0.001$  eV.<sup>17</sup>

The Na 2s spectrum of NaF taken at 300 K is shown in Fig. 4. The data appear to exhibit a substantial lifetime

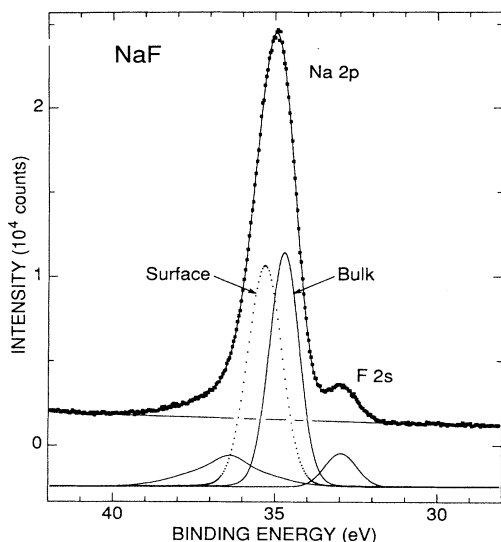


FIG. 3. Na  $2p$  photoemission spectrum of NaF at 300 K, fitted with bulk and surface components. Data were taken with 80-eV radiation. The overlapping F  $2s$  photopeak and the surface component arising from F photodesorption are also indicated.

width, but the actual value depends critically on the shape of the background. Wide-scan spectra also suggest that the background has negative curvature under the Na  $2s$  line because a combination of multiple plasmon losses, which are associated with the stronger Na  $2p$  photoemission, coincide at the energy of the Na  $2s$  line. In order to see this curved background and large lifetime width more clearly, we show in Fig. 4 the result of a fit using just a single photopeak and an adjustable background. A life-

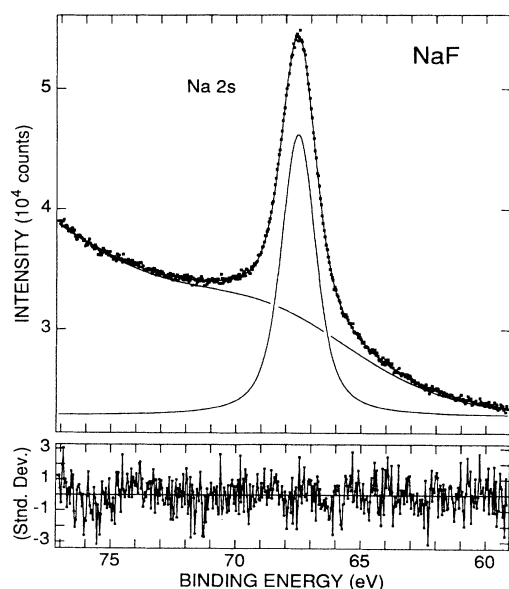


FIG. 4. Na  $2s$  photoemission spectrum of NaF at 300 K, fitted initially with only a single Voigt function profile to illustrate the need for a curved background. Data were taken with 110-eV radiation.

time width of 0.91 eV and a phonon width of 1.07 eV are obtained. The phonon width is slightly larger than that found in the Na  $2p$  data. The residuals show only weak systematic fluctuations, indicating that a fit containing both surface and bulk components would fail to converge unless various constraints are imposed. Attempts at such fits give smaller width parameters, but a unique solution was not obtained. Constraining the phonon width and surface-ion core-level shift to the values from the Na  $2p$  data leads to a reduced  $2s$  lifetime width of 0.75 eV and a probable error of  $\pm 0.15$  eV. This width compares reasonably well with the theoretical value of 0.64 eV.<sup>6</sup>

While the main subject of this work is the determination of interatomic Auger transition probabilities in sodium halides, it is useful to look at a related system in which such transitions are energetically forbidden, e.g., RbBr. This will establish limits on our ability to detect a small lifetime width in the presence of a much larger phonon width and thus help to evaluate the reliability of our analytic methods and results. Figure 5 shows data taken with He II radiation from the Rb  $4p$  states of RbBr at 300 K. In this case, the Br  $4s$  line is hidden in a part of the Rb spectrum where it does not interfere with the determination of the Rb bulk  $4p$  lifetime width. This case also differs from the sodium halides in that the Rb  $4p$  spin-orbit splitting is larger than the surface-ion core-level shift. Since the magnitude of the splitting is not known for ionic Rb salts, it was left as a free parameter. The analysis yields a spin-orbit splitting of  $0.909 \pm 0.005$  eV, very close to the value of 0.915 eV obtained for the free ion from atomic spectra,<sup>18</sup> but significantly larger than the splitting of  $0.856 \pm 0.003$  eV in metallic Rb.<sup>19</sup> The phonon broadening here is reliably determined to be

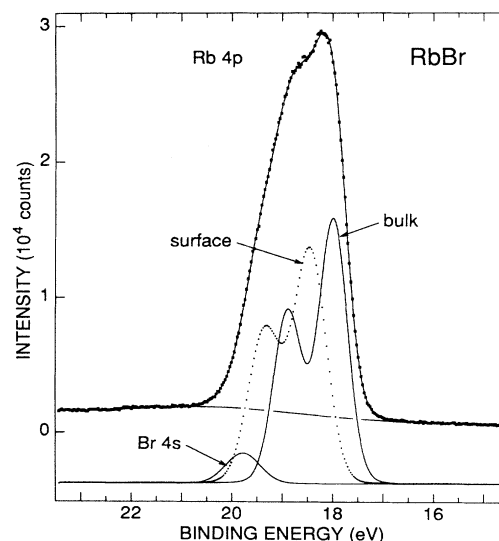


FIG. 5. Rb  $4p$  photoemission spectrum of RbBr at 300 K, fitted with bulk and surface components. Data were taken with 40.8-eV radiation. The spin-orbit splitting of Rb  $4p$  is larger than the energy shift between bulk and surface contributions, yielding well-defined fitting parameters. These results are used to demonstrate the reliability of analysis methods applied to the sodium halides.

0.65±0.01 eV, in excellent agreement with the theoretical value of 0.64 eV. The surface-ion core-level shift is similarly well determined: 0.47±0.01 eV. Limits on the lifetime width were obtained by fitting this spectrum with that parameter fixed to values covering the range from 0 to 0.12 eV. Satisfactory and barely distinguishable fits were obtained for  $0 < \Gamma_{4p} < 0.06$  eV. Larger values of  $\Gamma_{4p}$  led to significant deviations in the residuals. A small or vanishing lifetime width agrees with the expectations that a two-hole correlation energy of only ~1 eV is sufficient to prohibit interatomic transitions for a Rb 4*p* hole in RbBr.<sup>3</sup> We conclude that this example provides a good test of our ability to determine the magnitude of a small lifetime width in the presence of substantially larger phonon broadening.

The surface-ion core-level shifts obtained for the Na halides are 0.49±0.03 eV for NaBr, 0.48±0.03 eV for NaCl, and 0.60±0.04 for NaF. Values in the range 0.45±0.03 eV were previously obtained<sup>10</sup> for the chlorides, bromides, and iodides of K, Rb, and Cs. The slightly larger shifts found here for NaCl and NaBr are consistent with their smaller lattice constants, which lead to slightly larger contributions from the initial-state change in the Madelung potential at the surface.<sup>9,20</sup> The much larger shift found here for NaF, which has the greatest relative change in surface Madelung potential,<sup>9,20</sup> further supports the picture that the observed trends between different systems are due mainly to changes in the initial state, rather than from final-state screening.

#### IV. CONCLUSIONS

This investigation of the singly interatomic decay rates of the Na 2*s* levels in Na halides yields lifetime widths between 0.45 and 0.75 eV, confirming the importance of the interatomic process. The calculated results are, however, too small for NaCl (Ref. 5) and too large for NaF.<sup>6</sup> The fact that the Na 2*s* width in Na metal is as large as 0.28 eV (Ref. 15) is primarily due to the efficient nature of the Coster-Kronig decay process. The increased width in the insulators implies that the overlap of the Na 2*s* hole state with the 36 valence *p* electrons in the six neighboring halide ions is about two or three times the overlap with the conduction electrons of the metal in the presence of a core hole. The results obtained here for ionic materials are also compatible with earlier findings in the more covalent systems of GdB<sub>2</sub>, GdB<sub>4</sub>, and GdB<sub>6</sub>.<sup>21</sup> There, it was found that the Gd 4*f* lifetime width, which also decays by interatomic Auger processes involving B valence electrons, is as much as two or three times larger than the corresponding value in Gd metal.

Based on our findings for the 2*s* level, the enhancement of the doubly interatomic decay of the Na 2*p* hole state

might be crudely predicted to be of the order of  $(0.45/0.28)^2=2.6$  for the chloride and bromide and  $(0.75/0.28)^2=7.2$  for the fluoride. Since the Na 2*p* Auger lifetime width in the metal is 11 meV,<sup>17</sup> 2*p* widths of ~30 and ~80 meV, respectively, are to be expected for these materials. The average experimental results here of ~30 and ~100 meV do provide upper limits on  $\Gamma_{2p}$ , and are in reasonable agreement with these predictions, but the corresponding uncertainties of about 30 and 50 meV are too large to allow more quantitative evaluations.

Implications on the observation<sup>11,12</sup> of significantly enhanced lifetime widths of outermost *p* hole states in alkali metal atoms adsorbed on transition-metal substrates are unfortunately limited, because the relevant valence charge distributions are very different in the two cases. For the ionic salts, the charge is in the valence states surrounding the neighboring anions, while for alkali-metal atoms adsorbed on a metal the surface charge resides in a cloud between the substrate and the adsorbate,<sup>22,23</sup> resembling<sup>12</sup> a covalent bond. In the particular system of Na adsorbed on W(110), a 2*p* lifetime width of 0.115±0.014 eV was found,<sup>12</sup> which is about ten times larger than  $\Gamma_{2p}$  in the metal. Thus, it appears that the single charge in the localized cloud has about as large an effect on the Na 2*p* lifetime width as that from the valence charge of six neighboring polarizable F<sup>-</sup> ions in NaF. The effect is even larger than that from the six anions in NaCl or NaBr.

We have previously pointed out<sup>12</sup> that if the localized charge cloud is composed of hybridized Na 3*s* and 3*p* character, the tenfold increase in Auger rate relative to that in Na metal is readily accounted for. The possible importance of interatomic Auger transitions as an alternative explanation was considered and believed to be too small based on the calculations of Ref. 4. From the present results, it is tempting to argue that the doubly interatomic Auger rate for an adsorbed atom would indeed be small because the number of neighboring atoms is further reduced at the surface. However, this argument would hold only if the neighboring atoms in the substrate were ions, as in the halides; it cannot be expected to hold for a metallic substrate. Here, calculations of interatomic Auger rates might well shed light on this question. The fair to good agreement between theory and experiment found in this work for NaCl and NaF should encourage such calculations.

#### ACKNOWLEDGMENT

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