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## Anharmonic surface vibrations in photoemission from alkali metals

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The phonon widths of outermost core-electron photoemission spectra from (110)-oriented overlayers of Na, K, and Rb metals show the expected Debye behavior for the bulk atoms, but significant deviations for the surface atoms. The data indicate a softening of the surface vibrational mode above 200 K. This effect, which is weak in Na but strong in K and Rb, demonstrates that the vibrational mode normal to the surface is anharmonic.

### I. INTRODUCTION

It has long been recognized that the vibrations of atoms in the surface of a bulk solid are anisotropic,<sup>1-4</sup> with a larger amplitude normal to the surface. This generalization is not valid when foreign atoms are adsorbed on the surface. More recently, surface anharmonicity has been invoked to explain many different observations, including increased thermal expansion of the surface layer,<sup>5</sup> loss of intensity of surface (inverse) photoemission peaks,<sup>6-8</sup> and anisotropic Debye-Waller damping in surface extended x-ray-absorption fine structure from adsorbates<sup>9-11</sup> and adsorbate-covered metal surface atoms.<sup>12</sup> Thermal effects on the intensity of He-atom scattering peaks from the Cu(110) surface have been variously attributed to thermal roughening<sup>13</sup> and surface anharmonicity.<sup>14</sup> The latter effect has recently been observed in electron-energy-loss data from that surface.<sup>15</sup>

Here, we present the results of a photoemission study of alkali metals in which the effects of anharmonicity on phonon widths of the surface-atom peaks clearly emerge. Following up on our demonstration of a soft phonon mode normal to the surface of Na,<sup>16</sup> we have extended our study to K and Rb over the same temperature range. The main difference between Na and these two heavier alkalis lies in their smaller cohesive energy and larger vapor pressure. We find, for all three metals, anharmonicity of the vibrational mode associated with surface atoms moving normal to the (110) surface. This anharmonicity, which becomes apparent in our measurements at temperatures greater than half of the melting point, is the result of anisotropic mode softening implicit in the desorption channel for surface atoms.

### II. EXPERIMENT

The alkali-metal samples were prepared by condensation of metal vapor, obtained from commercial SAES Getters sources, onto a Ni(100) substrate cooled to 78 K.<sup>16</sup> Low-energy electron diffraction (LEED) from the Na sample showed a single-domain (110) orientation.<sup>15</sup> LEED from the K films showed no long-range order. The lack of observable LEED features for K in this temperature range is attributed to thermal broadening, since a K film at 20 K, prepared as in this work, exhibits a well-

defined (110) diffraction pattern.<sup>17</sup> LEED observations of the Rb sample were not made. However, the core-level data, which exhibit only two peaks, are indicative of (110) orientation for this surface as well.

Photoemission data were obtained on the AT&T Bell Laboratories-University of Oregon 6m toroidal grating monochromator beam line at the National Synchrotron Light Source. The photoelectron energy distributions were measured with a 100-mm Vacuum Science Workshop hemispherical analyzer operated with a pass energy of 2 eV, yielding nominal resolutions of 40 meV. The monochromator resolution was in the range from 50 to 80 meV, depending on photon energy, giving total instrumental resolutions in the range of 65-90 meV. Ambient pressure was in the range of  $(1-2) \times 10^{-10}$  Torr, dominated by H<sub>2</sub>. The temperature-dependent data were taken while the substrate warmed up over a period of 2 h, up to the point where desorption becomes appreciable, i.e., up to a vapor pressure of  $3 \times 10^{-11}$  Torr.

### III. RESULTS AND DISCUSSION

The data were analyzed by fitting them with spin-orbit (SO) doublets made up of Doniach-Šunjić<sup>18</sup> lines. The background was represented by a sloping line and a power-law term. We initially assumed that the bulk and surface SO splittings are the same, and that the natural lifetime widths of the  $p_{3/2}$  and  $p_{1/2}$  core holes at the surface are the same as in the bulk. Only in the case of Rb, where the four SO lines are resolved at low temperature, was it necessary to modify one of these assumptions, namely that regarding the SO splitting. The data convincingly show that the surface SO splitting is 10 meV smaller than that of the bulk. For Na and K, in which the bulk  $p_{1/2}$  and surface  $p_{3/2}$  lines overlap, the bulk SO ratio was constrained to the statistical value of 0.5 because it could not be determined from the data. The singularity indices and Gaussian widths of the bulk and surface components were assigned independent values from previous work.<sup>19</sup>

In order to determine the best value for such parameters as the natural widths, singularity indices, surface-atom core-level shift, and SO splitting, all of which are clearly temperature independent,<sup>20</sup> we first fit the entire set of temperature-dependent data for each metal without

constraints beyond those already mentioned. By progressively constraining those parameters which are independent of temperature, we arrive at a set of values which yields satisfactory fits to all the data when only the bulk and surface Gaussian widths remain free. The parameters used in the final analysis are summarized in Table I. This iterative procedure reduces the errors in the Gaussian width due to the coupling with other parameters, which becomes increasingly troublesome at the higher temperatures.

Analysis of a representative K  $3p$  spectrum is illustrated in Fig. 1. The data, taken at 172 K, were fitted using the parameters in Table I, and are one of a series of data sets taken as a function of temperature. The SO splitting obtained in this analysis is found to be identical to the value for the neutral K atom with  $3p^5 4s^2$  configuration,<sup>21</sup> indicating that the  $3p$  hole in the metal is fully screened. The value of the surface-atom core-level shift has been confirmed by SO stripping data taken at higher photon energy. The larger  $p_{1/2}$  lifetime width relative to that for the  $p_{3/2}$  state is due to Coster-Kronig transitions, while the larger singularity index for the surface atoms is due to increased contribution of  $s$ -wave scattering in the narrower, more atomiclike surface conduction band.<sup>19</sup> The only unusual aspect of the K data is the nonstatistical SO ratio for the surface atoms. This ratio has been found to depend on the photoelectron take-off angle, a phenomenon not unique to this metal and one that is presently not understood.

Representative results for the Rb  $4p$  data taken at 147 K are illustrated in Fig. 2. The parameters for Rb in Table I are in good agreement with those recently obtained from data taken with He II resonance radiation.<sup>22</sup> The Na data of Ref. 16, including additional data obtained at higher temperatures, were reanalyzed using the method described here, yielding results very similar to those reported in that earlier work.

The total Gaussian widths for the bulk and surface components in the three metals are plotted in Fig. 3 as the square of the width versus temperature. This presentation is motivated by the high-temperature expansion of the expression for the phonon width in the Debye model.<sup>16</sup> For temperatures above the Debye temperature,  $\Theta_D$ , the total measured Gaussian width  $G_{\text{tot}}$ , including

TABLE I. Binding energies, surface-atom core-level shifts, and line-shape parameters used in the analysis of the Na, K, and Rb spectra.

	Na	K	Rb
Binding energy (eV)	30.6	18.34	14.93
Surface shift (meV)	184	175	182
Natural width $p_{3/2}$ (meV)	12	14	20
Natural width $p_{1/2}$ (meV)	12	50	95
Singularity index (bulk)	0.16	0.14	0.14
Singularity index (surface)	0.20	0.21	0.22
SO splitting (bulk) (meV)	160	257	856
SO splitting (surface) (meV)	160	257	846
SO ratio (bulk)	0.50	0.50	~0.52
SO ratio (surface)	0.56	0.60	~0.55

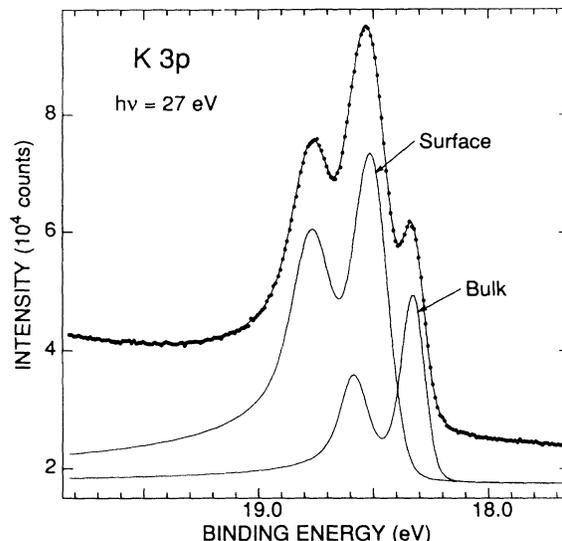


FIG. 1. Analysis of the photoemission spectrum of the  $3p$  region of K metal. The data, taken with the sample at 172 K, are one of a set used to determine the temperature dependence of the phonon width. The bulk and surface spin-orbit doublets, together with a power-law background (not shown), produce the line through the data points.

contributions from the instrumental resolution  $G_{\text{res}}$ , is approximately given by

$$G_{\text{tot}}^2 = G_{\text{res}}^2 + G^2(0) \frac{8}{3} \frac{T}{\Theta_D} \left[ 1 + \frac{1}{2} \left( \frac{3}{8} \frac{\Theta_D}{T} \right)^2 + \dots \right] \quad (T > \Theta_D), \quad (1)$$

where  $G(0)$  is the Gaussian width from the phonon broadening at  $T=0$  K. For  $T > \Theta_D$ , the second term in

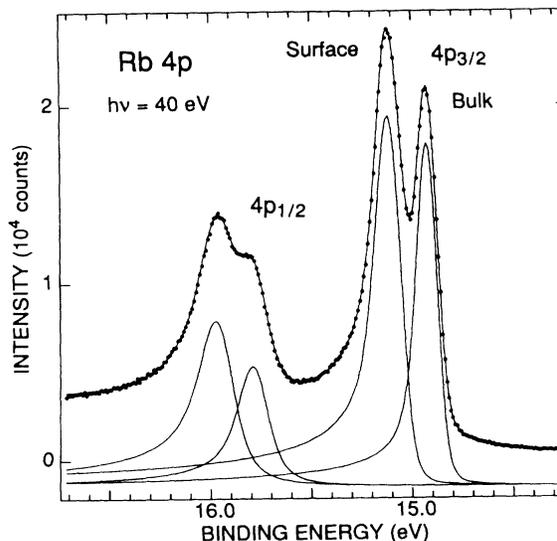


FIG. 2. Analysis of the photoemission spectrum of the  $4p$  region of Rb metal. The data, taken with the sample at 147 K, are one of a set used to determine the temperature dependence of the phonon width. The components of the bulk and surface spin-orbit doublets are shown separately.

square brackets is smaller than 0.07. Such a plot should therefore be linear for temperatures greater than the corresponding Debye temperatures, which for Na, K, and Rb are 155, 100, and 50 K, respectively. The linearized form of Eq. (1), i.e., neglecting the second term in the square brackets, extrapolates to an intercept at  $T=0$  equal to the square of the instrumental resolution.

For all three metals, the bulk Gaussian width exhibits the expected linear increase of  $G_{\text{tot}}^2$  with temperature. This affirms our methodology for obtaining Gaussian widths from the data. The lines drawn through the bulk widths are the results of linear least-squares fits to the data points. The fact that the intercepts of these lines at

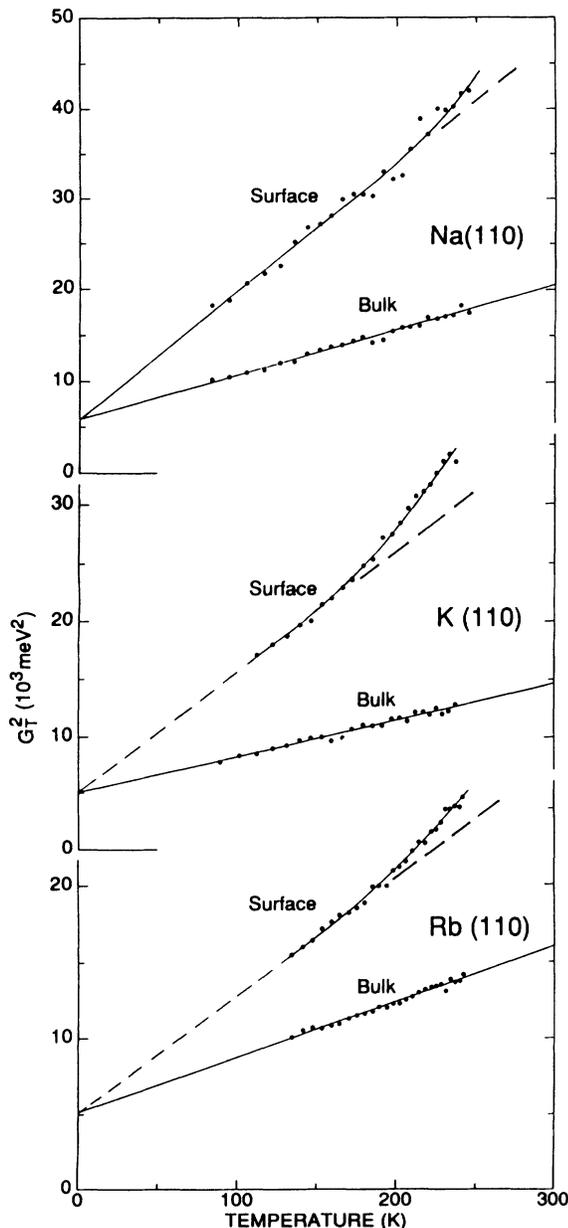


FIG. 3. Square of the total Gaussian width of bulk and surface  $np$  spin-orbit doublets of Na, K, and Rb ( $n=2, 3$ , and 4, respectively) plotted against temperature. The straight lines through the bulk data are the results of least-squares fits. The curved lines through the surface data are guides to the eye.

$T=0$  are all close to the square of the instrumental resolution, independently measured from the width of the Fermi cutoff, confirms the validity of Eq. (1).

Because the data for Na start below  $\Theta_D$ , it is desirable to compare a fit to the data using the more general expression for the phonon width,<sup>23</sup>

$$G^2(T) = G^2(0) \left[ 1 + 8 \left( \frac{T}{\Theta_D} \right)^4 \int_0^{\Theta_D/T} \frac{x^3 dx}{e^x - 1} \right]. \quad (2)$$

The result is shown in Fig. 4 together with the high-temperature, linearized asymptotic form from Eq. (1). It is clear that a fit with a straight line results in only a small overestimate of the intercept. For K, with a smaller  $\Theta_D$ , the separation between the fit using Eq. (2) and that using Eq. (1) is smaller than the scatter of the data.

The fit to the bulk Na data in Fig. 4 yields a more reliable value for the zero-temperature phonon width than can be obtained with the high-temperature expansion in Eq. (1). The resulting value of 54 meV is in reasonable agreement with the theoretical estimate of 65 meV.<sup>24</sup> The extrapolated phonon width at 300 K from Fig. 4 is 124 meV, slightly larger than the semiempirical value of 106 meV obtained by Flynn.<sup>24</sup> A similar fit to the K data (not shown) yields a zero-temperature phonon width of 32 meV and a 300-K width of 91 meV. The extrapolated phonon width in Rb at 300 K from Fig. 3 is 104 meV. The room-temperature widths for K and Rb are in good agreement with those obtained from soft-x-ray emission edges.<sup>25</sup> These results for the bulk phonon widths confirm that our method of data analysis successfully separates the instrumental and lifetime widths from the phonon contribution and gives confidence to our analysis below of the surface phonon width.

At higher temperatures, the surface Gaussian widths deviate from the expected linear behavior for all three metals. In Na this deviation is relatively small, but in K and Rb the deviations are much more pronounced. This

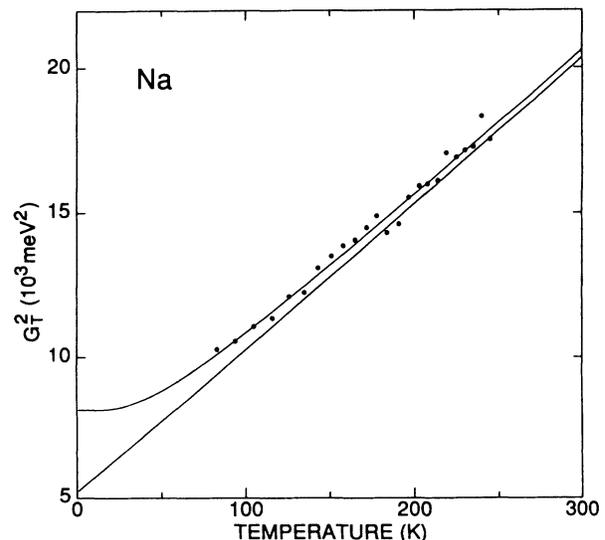


FIG. 4. Fit to the bulk Gaussian width of Na using Eq. (2) (see text).

upward curvature is not compatible with Debye theory, in which the square of the phonon width increases linearly with temperature above the Debye temperature. In view of the smaller Debye temperature (larger slope) of the plot of the square of the surface Gaussian width versus temperature, there is no need to invoke Eq. (2), even for Na. In terms of the Debye model, the deviations can be thought of as being due to a decrease of  $\Theta_D$  for surface atoms at elevated temperatures, and likely involves a softening of the mode normal to the surface. The softening begins around 200 K in Na and 150 K in K and Rb, or about half the bulk melting point.

The softening at large excitation is a result of the weak restoring force for excursions away from the surface, and so is directly related to the desorption channel of the surface atoms. For Na, K, and Rb, the vapor pressure reaches  $3 \times 10^{11}$  Torr at 300, 255, and 240 K, respectively. Anharmonicity becomes apparent well below these temperatures. The surface anharmonicity is much greater than that in the bulk because the surface potential contains large odd-power terms to express the asymmetry of the restoring force for displacements toward and away from the surface.

#### IV. CONCLUSIONS

The phonon widths of core-electron photoemission spectra from atoms in the first atomic layer of alkali metals give evidence for a softening of the vibrational mode normal to the surface for temperatures above one-half the bulk melting point. The softening reflects the asymmetry of the potential well, being shallower for displacements away from the surface than for those toward it. The resulting anharmonic vibrations also correlate with vapor pressure, which in turn depends on the potential-well depth in desorption.

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