Strong Phonon Replicas in Be 1*s* Photoemission Spectra

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The Be 1*s* core level photoemission line from metallic Be is shown to contain unexpected internal fine structure. We argue that this fine structure is caused by intrinsic excitation of a narrow band of optical phonons in the 1*s* photoemission process. The general importance of the present results for high resolution core level photoemission investigations of metals is pointed out.

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Core level photoemission is a well-established and frequently used experimental technique for investigating the surface region of solids [1]. Much of the applicability of the technique derives from the fact that the core level binding energy of an atom experiences small shifts if the surroundings of the atom changes [1,2]. Because of this so-called "chemical shift" effect, the technique may be used to distinguish atoms which occupy inequivalent sites and thereby experience different local electronic structures. The detailed line shape of the core level peaks also contains information on the local electronic structure of the photoemitting atom [1,3]. Today, the ultimate experimental resolution is often better than the natural linewidth of the investigated core levels, thereby providing excellent opportunities for studying small binding energy shifts and detailed line shapes. A full understanding of the various mechanisms that may cause shifts of core level binding energies is important for fully exploiting this favorable experimental situation. One example of a mechanism that may cause binding energy shifts and create multiple components is excitation of localized internal molecular vibrations when a chemisorbed molecule is core ionized [4,5]. Incorrect line shape parameters are derived if this effect is not included. Vibrationally caused resolvable multiple components in core level spectra are not limited to chemisorbed molecules with their intrinsically localized vibrations. In this Letter, we present experimental evidence that, when measured at sufficiently high energy resolution, the Be 1*s* core level photoemission line appears not as a single line but instead as a structure composed of a number of individual peaks. We argue that this is due to the excitation of phonons during the photoemission process. Similar effects are expected also for other solids, and explicit inclusion of them is vital in any detailed analysis of the core level line shape from solids.

The measurements were performed at beam line I311 [6] at the MAX II storage ring, Lund. Sweden. The total (photons + electrons) energy resolution in the present high resolution measurements was around 20 meV. All measurements presented here were made at a sample temperature of 100 K and at normal emission. The Be(0001) surface was cleaned as previously described [7,8] and was found to give excellent low energy electron diffraction patterns indicating good ordering of the surface region.

In Fig. 1, we show Be 1*s* spectra from a Be(0001) surface measured at two different resolutions. The total resolution in the lower spectrum is about 70 meV, that is, comparable to what was achieved in earlier studies [7,8] of Be(0001). Also included in Fig. 1 is a decomposition of this lower resolution spectrum into Doniach-Šunjić (DS) line shapes [9] convoluted by a Gaussian. As demonstrated previously [7,8,10,11], these components derive from individual layers of the Be(0001) surface; component B is the emission from bulk layers whereas components SX ($X = 1$–4) are due to emission from the Xth layer [12]. The upper spectrum of Fig. 1 is measured at a resolution of just above 20 meV. As expected, this spectrum shows the just-mentioned components due to emission from the different layers. The improvement in resolution, however, does not simply lead to a sharpening of these components but, in addition, causes an unexpected

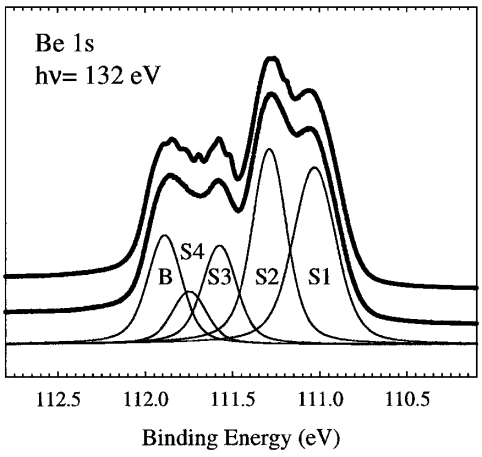

FIG. 1. Be 1*s* spectra from Be(0001) at $h\nu = 132$ eV. Total resolution is ~70 meV in the lower and ~20 meV in the upper spectrum. A decomposition of the lower spectrum into components from the first four (S1–S4) and the bulk (B) layers is included.

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fine structure to appear. As seen from Fig. 1, all but the first layer component contain this fine structure. The observed fine structure is not confined to spectra from the Be(0001) surface but is also observed [13] in Be 1s spectra from Be(10$\bar{1}$0) and Be(11$\bar{2}$0) surfaces. The fine structure seen in Fig. 1 thus seems to be a fundamental property of the 1s line shape in photoemission from Be metal.

The fine structure can be reproduced if each of the layer components is taken to consist of a number of components having slightly different binding energies. For the surface layer, no fine structure is visible and this layer is well described by a single broad component. When examining the experimental spectra, a binding energy difference of just below 60 meV between the fine structure components (from the same layer) was frequently found. We therefore modeled the emission from each layer by the sum of seven DS line shapes [9] (convoluted by a Gaussian) positioned equidistant in binding energy; $E_B(i) = E_B(0) + i^*\Delta E$, $i = 0$ to 6, where $\Delta E \sim 58$ meV. The relative intensities of the seven components can be constrained by noting that broadening of this "high resolution line shape" should result in a line shape similar to the one derived for lower resolution spectra. The inset of Fig. 2 shows the line shape

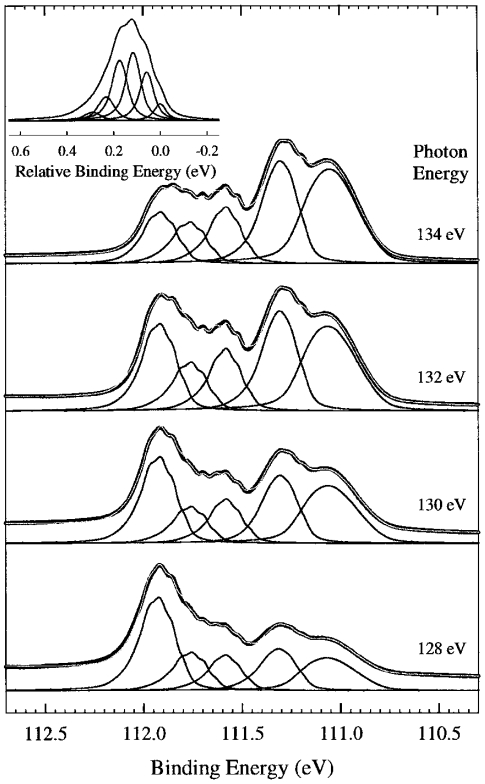

FIG. 2. Be 1s spectra from Be(0001) at the indicated photon energies. Experimental data are shown as thick black lines. Components from the first four and the bulk layers are shown by thin black lines and the resulting fit is shown as light grey lines which closely overlap the experimental data. Inset shows the generic line shape (see text) used for all but the surface layer.

for a single Be layer constructed in this way, using parameter values appropriate for the bulk emission. The quality of the fits obtained by use of this line shape is illustrated in Fig. 2 by a number of Be 1s spectra measured at photon energies between 128 and 134 eV and fits of these. The parameter values used in the fits will be discussed below. As seen, good fits may be obtained for both bulk (128 eV spectrum) as well as surface sensitive spectra (134 eV spectrum). It should be noted that, whereas the line shape varies slightly between the individual layers, the line shape for an individual layer is kept constant when fitting the spectra at different photon energies. Finally, we note that the line shape in Fig. 2 also provides good fits of Be 1s spectra [13] from Be(10$\bar{1}$0) and Be(11$\bar{2}$0) surfaces.

We believe that the observed fine structure is caused by excitation of phonons in the 1s ionization process. In the case of metals, excitation of phonons is commonly assumed to yield a structureless contribution to the broadening of the photoemission line shape [1,3,14]. In the limit of excitation of many phonons, this broadening is well described by a Gaussian [1,3,14,15]. However, this treatment of the phonon broadening may be misleading if the phonon density of states contains pronounced structure. One example of this is chemisorbed molecules where excitation of the localized internal molecular modes in the photoemission process has been theoretically predicted [16] and experimentally shown [4,5] to result in the creation of a number of replica lines; that is, the observed photoemission line consists of a number of individual components. Furthermore, the intensity distribution of these components is experimentally found [4,5] to follow a Poisson distribution as expected from the so-called linear coupling model [17]. The phonon spectrum of Be metal [18] stretches up to $\sim$80 meV and contains pronounced structure in the 50–80 meV range due to optical phonons. By analogy to the case of internal molecular vibrations, one would expect that excitation of a narrow band of optical phonons with energies close to 58 meV would create fine structure in the Be 1s spectrum and thus explain the experimental observations. In order to test this more quantitatively, we calculated broadening functions using a simple model for the core hole-phonon coupling. In a linear coupling model [15,17], the phonon broadening function is determined by a function $g(\omega)$ involving the linear coupling coefficients $B_{\mathbf{q}\nu}$ for phonon mode $(\mathbf{q}, \nu)$, $g(\omega) = (1/\omega^2)\sum |B_{\mathbf{q}\nu}|^2 \delta(\omega - \omega_{\mathbf{q}\nu})$. The first few moments of $g(\omega)$ give the relative strength $\exp(-\bar{n})$ of the no-phonon line ($\bar{n}$ is the mean number of shakeup phonons), the lattice relaxation energy ε_0, and the rms width Δ; see, e.g., Ref. [15]. We used a model $g(\omega)$ function composed of two Gaussians centered at ω_1 and ω_2 and multiplied with an overall factor to ensure the correct low-frequency behavior $\propto \omega^3$. One Gaussian (ω_1) simulates the coupling to optical phonons and was chosen rather narrow, and the other (ω_2) simulates the

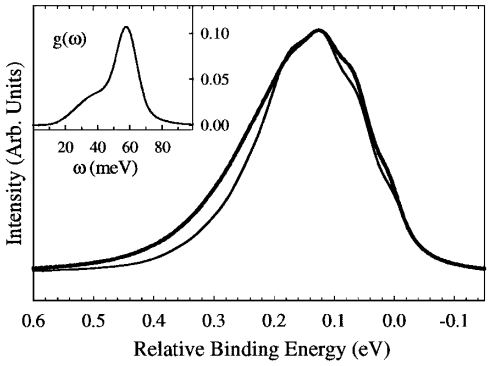

FIG. 3. Comparison between the bulk component (thin line) from Fig. 2 and the best fit theoretical line shape (thick line). Inset shows the resulting effective $g(\omega)$ function (see text).

acoustical phonons and was chosen rather broad. The overall strength is constrained by the experimental width of the total emission from a single layer, and ω_1 is determined by the observed separation ($\sim$58 meV) of the fine structure components. The theoretical line shape also includes a lifetime broadening of 50 meV [we give all widths as full width at half maximum (FWHM)], a Mahan-Nozières-DeDominics (MND) [19] asymmetry $\alpha = 0.02$, broadening [20] from thermal particle-hole excitations at $T = 100$ K, and a Gaussian broadening of 20 meV representing the experimental resolution. In Fig. 3, we compare the optimum theoretical broadening with the experimental bulk component. The corresponding $g(\omega)$ is shown as an inset. The spectrum in Fig. 3 corresponds to a lattice relaxation energy of 140 meV, and $\overline{n} = 2.8$. These model calculations agree with the above expectations based on analogy with the case of internal molecular vibrations. The optical phonons give a no-phonon line and a number of phonon replicas separated by ω_1 and of increasing widths and with weights which follow a Poisson distribution. The nth replica is an n-fold self-convolution of the optical-phonon part of $g(\omega)$ (this is also the case for the acoustical phonons, however, these self-convolutions overlap and usually build a broad Gaussian-like structure), and thus the widths of the replicas increase as the square root of their order. This differs from, e.g., the molecular case where all replica have the same width because the excited molecular vibrations can be considered infinitely sharp in energy. In light of the admittedly simple model of the phonon structure used, we find the agreement between the bulk line shape and the theoretical line shape shown in Fig. 3 satisfactory. A better quantitative agreement would presumably require going beyond linear coupling.

We now return to the fittings of the experimental spectra. As mentioned, the emission from each layer (except the surface layer which shows no observable fine structure) is modeled by a number of equidistant DS line shapes [9] (convoluted by Gaussians) representing the phonon replicas, $E_B(i) = E_B(0) + i^*\Delta E$, where ΔE is a constant for each layer. In view of the large number of replicas and the considerable overlap between the layer components, constraints have to be applied in order to limit the number of free parameters. In addition to requiring that the replicas are equidistant in energy, we required that their relative intensity distribution is similar for the different layers. Determination of separate Lorentzian (LW) and Gaussian (GW) widths of the replicas is highly ambiguous for the present spectra, and we therefore kept LW fixed at 50 meV for all layers and only optimized GW. The analysis showed that GW had to increase with replica number. In view of the above theoretical results, we used the following form for the Gaussian FWHM GW(i) of the ith replica, $\mathrm{GW}(i) = \mathrm{GW}(0) + \sqrt{i^*}\,\Delta\mathrm{GW}$. The MND [19] asymmetry parameter, α, was kept equal for all layers. Finally, when fitting spectra measured at different photon energies, the only adjustable parameters are the total intensities of the various layer components. As the surface sensitivity varies strongly with photon energy (see Fig. 2), this provides strong limits on the possible line shapes of the different layers. Optimum values for the parameters are given in Table I.

The present results clearly show that line shape parameters derived without inclusion of the phonon replicas have little physical relevance. Previous analysis of lower resolution Be 1s spectra have resulted in GW values of $\sim$200 meV [7,8] (including the experimental contribution) and LW values of $\sim$70 meV [8] or $\sim$90 meV [7]. When using the line shape in Fig. 2, we find that the total FWHM of the sharpest individual components has to

TABLE I. Parameter values used for the decompositions (see text) in Fig. 2 for the second to the fourth surface layer (S2–S4) and for the bulk layer B. $E_B(0)$: binding energy of the zero phonon line, ΔE: energy split of the phonon replicas, I_i: Relative intensity of the ith phonon replica, G(0): Gaussian FWHM applied to all components. A Lorentzian FWHM of 50 meV, an MND asymmetry index α of 0.02, and an increment of the Gaussian FWHM with the square root of phonon replica number, $\Delta G(i)$, of 13 meV were used for all layers.

	$E_B(0)$ eV	ΔE meV	I_0 %	I_1 %	I_2 %	I_3 %	I_4 %	I_5 %	I_6 %	G(0) meV
S2	111.186	58 ± 2	8	23	31	24	10	3	1	41 ± 4
S3	111.460	57 ± 2	7	20	33	26	9	4	1	24 ± 3
S4	111.636	58 ± 2	6	21	31	26	10	4	1	22 ± 3
B	111.797	59 ± 2	6	20	30	27	11	4	1	26 ± 3

be below ~70 meV in order to reproduce the fine structure. Thus, the previously [7,8] derived LW and GW are too large. The present value of LW agrees well with the value of 40 meV for bulk Be calculated by Almbladh and Morales [21]. The MND asymmetry index is found to be small (~0.02 ± 0.02) in agreement with the low density of states at the Fermi level for Be metal.

The energy split between the replicas, that is the average energy of the excited optical phonons, is for all layers close to 58 meV. We are unable to detect any significant differences among the layers. When comparing to the phonon spectrum of Be [18], this number seems reasonable. The large intensities found even for highly vibrationally excited states are also understandable. The core-hole-lattice coupling reflects directly the core-hole-induced forces on neighboring sites, or, alternatively, the changes in equilibrium positions when a static core-hole impurity is introduced. In the case of 1*s* photoemission of metallic Be, Feibelman [22] has argued that the final state Be atom has a distance to its nearest neighbor Be atoms which is ~0.3 bohr larger than the equilibrium distance. Such a large misfit corresponds to a quite strong coupling to the lattice.

The emission from the second layer, S2, shows a significantly larger Gaussian width than the deeper layers. This is presumably caused by the unusual properties of the Be(0001) surface; strong surface states are known [23] to exist and make the surface layer(s) more free electronlike and also the ground state vibrational properties of the surface layers differ [24] from those of bulk layers. Furthermore, it may be noted that steps and vacancies are expected to be more abundant in the surface layer, and therefore a larger disorder related broadening is expected for near surface layers. The lack of any resolvable structure in the surface layer emission is also understandable from the above reasoning. Furthermore, the possibility of a larger lifetime width of the surface emission caused by an increased valence electron density at the surface [23] should be kept in mind. ΔGW is found to be 13 ± 3 meV for all layers. This implies that the band of optical phonons to which the core hole couples has an energy spread of about 13 meV.

In summary, we have shown that Be 1*s* spectra from metallic Be exhibits an unexpected fine structure. These structures were argued to be caused by excitations of optical Be phonons in the photoemission process, and it was briefly discussed how the experimental observations fulfilled expectations concerning intensity and width for such phonon replicas. Whereas these phonon replicas may be particularly strong in Be metal because of the large size misfit [22] between neutral and core-ionized Be, they are nevertheless to be expected in other metals as well.

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