# Calorimetry at Surfaces Using High-Resolution Core-Level Photoemission

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(Received 17 March 2004; published 3 September 2004)

We have developed a method to measure simultaneously the internal energy of bulk and the first layer atoms of a crystal. The internal energy of bulk and the surface atoms of lithium (110) have been evaluated from 22 K up to above the melting transition, applying the Debye model to the thermal broadening of the respective 1*s* photoemission lines. Our measurements clearly reveal two phase changes: the known liquid to solid transition and the surface melting, occurring 50 K below the bulk melting point.

DOI: 10.1103/PhysRevLett.93.106105 PACS numbers: 68.35.Md, 65.40.–b, 79.60.–i, 79.90.+b

Because of the research and development activities on nanostructure science explosively growing in the last years, the need to probe the surface thermodynamic properties has become today one of the issues of condensed matter physics. At present, though, since standard calorimetric techniques are sensitive to the bulk properties, but cannot recognize the surface contribution, the surface thermodynamics is far from being characterized. Here we show how high-resolution core-level photoemission can be used to perform surface calorimetry. As a pioneering application we measured the Li1*s* bulk and surface core-level line shape from 22 K up into the liquid phase. Like in many crystals, distinct and simultaneous investigation of bulk and surface atoms was allowed by the well distinguishable binding energies of the respective photoemitted core electrons. A quantitative one-to-one correspondence between the temperature-dependent broadening of the bulk photoemission peak and the calorimetric specific heat data has been established in the frame of the Debye model. Deriving a similar relationship for the thermal broadening of the surface core-level peak, the temperature-dependent surface internal energy of Li(110) has been obtained.

The measurements were performed in the ultra-high-vacuum (base pressure $<5 \times 10^{-11}$ mbar) experimental chamber of the SuperESCA beam line at ELETTRA. Li(110) films (about 60 Å thick) were grown *in situ* onto a clean Ni(100) crystal kept at 22 K. Li1*s* core-level photoemission spectra were obtained with a photon energy of 94 eV and the photoelectrons were collected at 40° from normal emission using a hemispherical electron energy analyser with an energy resolution of 80 meV. The sample temperature was changed and controlled using a filament behind the Ni substrate, ohmically heated by a 100 Hz square-pulsed current. The data were acquired in that part of the pulse cycle where the current was off. The temperature was measured by a calibrated thermocouple welded to the sample with incertitude of ±2 K. The experimental set-up allowed fast collection of Li1*s* core-level spectra (52 sec per spectrum) while changing the sample temperature from 22 K to 553 K, i.e., from the low temperature solid phase, across the bulk melting transition occurring at $T_M = 453$ K [1], up to about 100 K into the liquid phase. Lithium was chosen because its vapor pressure also allows performance of photoemission experiments in the liquid phase, thus investigating the possible occurrence of surface premelting, which in (110) surfaces of bcc crystals is still an open question [2]. Moreover, lithium is representative of the class of simple metals and is a good test case for different theoretical approaches to solid-to-liquid transition dynamics.

A selection of Li1*s* photoemission spectra as a function of temperature is shown in Fig. 1. Two main features characterize the spectra: the sharpest one, at lower binding energy, corresponds to the bulk atoms, the broader one at higher binding energy corresponds to surface atoms [3]. Already from the raw data, one clearly observes that the two peaks broaden as the temperature increases. Within the temperature range investigated, the main contribution to the temperature-dependent linewidth comes from the phonon distribution, while the excitation and distribution of electrons near the Fermi level is mainly responsible for the asymmetric line shape of the peaks, giving a tail at higher binding energies (Doniach-Sunjic line shape [4]). It is also worth noting that the binding energies, approximately corresponding to peak maxima, shift toward higher values as the temperature increases.

To obtain the temperature-dependent phonon contribution to the core-level linewidth we have fitted the Li1*s* core spectra using two Doniach-Sunjic functions, each one convoluted with a Gaussian function. The Doniach-Sunjic widths (representing the core-hole lifetime) and the asymmetry parameters were taken from refs. [3,5] and kept constant. The Gaussian width accounts for the phonon contribution and the temperature-independent instrumental resolution (80 meV). A third large peak has been used to reproduce the small oxide signal present in the low temperature spectra at higher binding energy. The

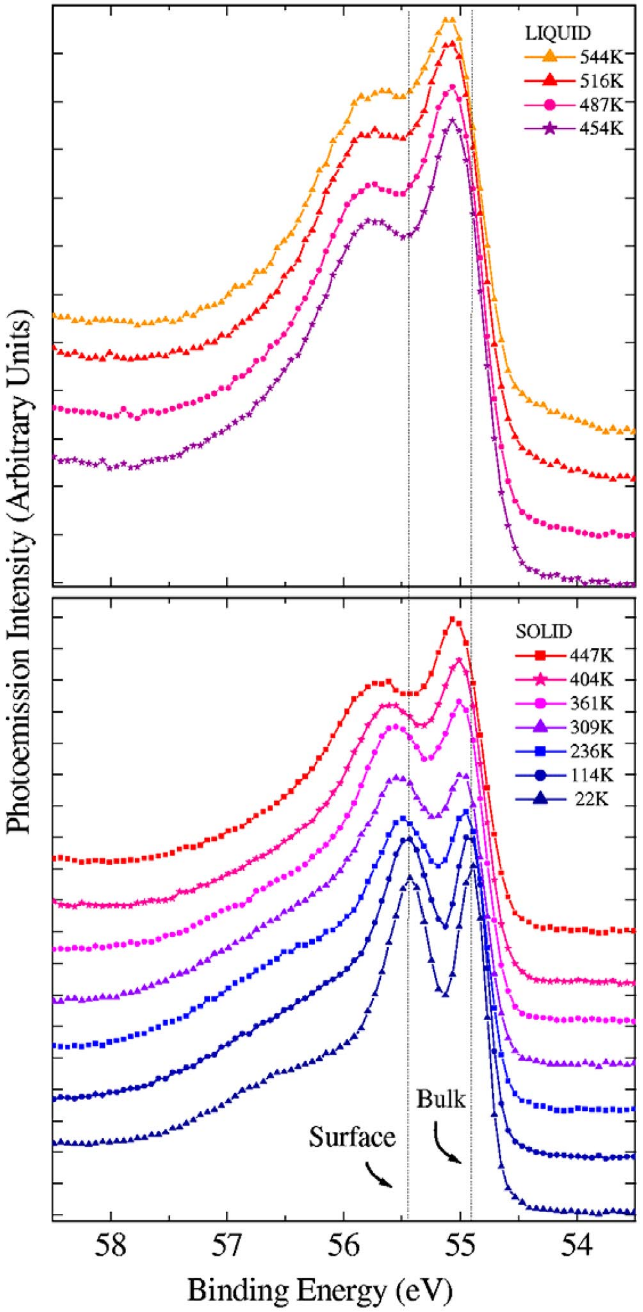

FIG. 1 (color online). Li 1*s* core-level photoemission spectra as a function of temperature. Upper Panel: bulk solid phase. Lower Panel: bulk liquid phase. Vertical dotted lines are guides for the eye. Because of residual water in the experimental chamber, an oxide peak appears in the low temperature spectra as a consequence of a partial surface oxidation. The presence of oxide (accounted for using a Gaussian peak in the fitting procedure) does not affect the results of this report.

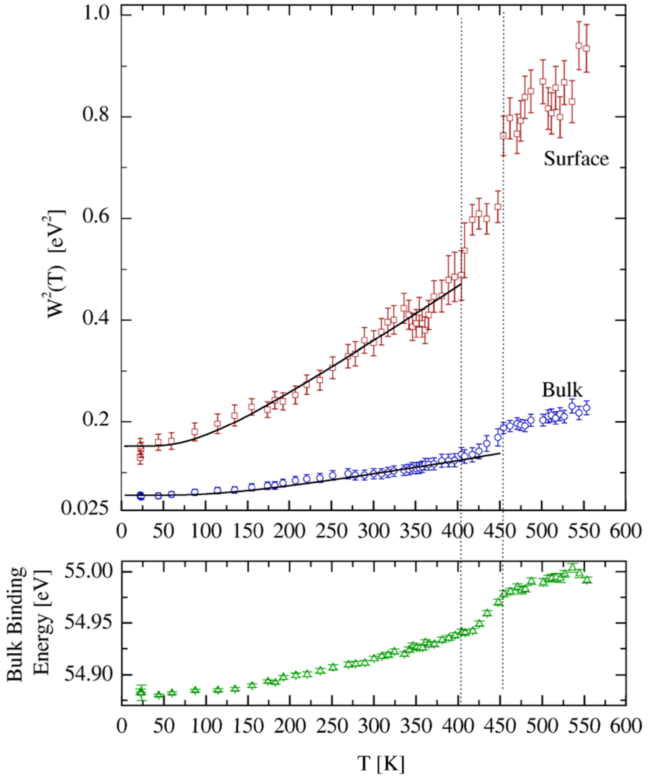

FIG. 2 (color online). Upper panel: Temperature dependence of the squared Gaussian contribution (phonon broadening) to the core-level linewidth for bulk (circles) and surface (squares) peaks. The corresponding best fits of core-level phonon broadening theory—Eq. (1) and Eq. (5) for bulk and surface, respectively—are superimposed as solid lines. Lower Panel: The thermal shift of the bulk peak binding energy.

background was taken in proportion to the spectrum integral.

For each spectrum, the fitting procedure returns the Gaussian width and the binding energy of bulk and surface components. Figure 2 shows the square of the temperature-dependent phonon contribution to the core-level linewidth extracted from the experimental data for bulk (circles) and surface (squares) peaks. Both core levels show a monotonic increase of the linewidth with temperature up to the occurrence of anomalies at $T^* = 404$ K and $T_M = 453$ K which are the hallmarks of phase transitions.

As the photo-emitted core-level electrons in molecules carry information about the phonon modes according to the Frank-Condon principle, in a similar way the photo-emitted core-level electrons in crystals carry information about the collective lattice vibrations [6,7]. The coupling between core electrons and phonons induces a temperature-dependent broadening of the corresponding photoemission lines, whose theoretical expression has been calculated by several authors for bulk atoms [7–10]. Here we use the general form obtained by Hedin and Rosengren [8] on the basis of the Debye model, according to which the squared phonon broadening $W^2$ is given by

$$W^2(T) = W_0^2\left[1 + 8\left(\frac{T}{\theta_D}\right)^4 \int_0^{\theta_D/T} dx \frac{x^3}{e^x - 1}\right] \quad (1)$$

where $\theta_D$ is the bulk Debye temperature and $W_0$ is the zero-temperature phonon width. This equation, which we tested down to the asymptotic region lying around 22 K and up to the melting transition, turned out an excellent fitting of our bulk solid-phase data. We obtained $\theta_D = 470 \pm 25$ K and $W_0^2 = 0.051 \pm 0.002$ eV$^2$, in good agreement with values estimated by experiments performed in a reduced temperature range (78–280 K )[3], and with the phonon spectrum of lithium [11]. We note that a similar value of $\theta_D$ has been found also in the liquid phase [12].

$W^2(T)$ is proportional to the phonon contribution to the internal energy $U(T)$ in the Debye model, whose analytical expression for a mole of bulk atoms is [13]

$$U(T) = \frac{9RT^4}{\theta_D^3}\int_0^{\theta_D/T} dx\,\frac{x^3}{e^x - 1} \tag{2}$$

where $R$ is the constant of perfect gases.

Comparing Eq. (1) and Eq. (2) we obtain

$$U(T) = -\frac{9R}{8}\theta_D + \frac{9R}{8}\frac{\theta_D}{W_0^2}W^2(T). \tag{3}$$

Equation (3), rigorously valid for a mole of bulk atoms, states that the measurement of the temperature-dependent core-level phonon broadening in photoemission experiments allows determining the internal energy of the investigated system. In Fig. 3(a) we show the quantitative good agreement between the published calorimetry measurements of the Li internal energy [1] and $U(T)$ as calculated from Eq. (3) using our bulk data (dots).

In order to further corroborate our core-level analysis, we also derived $U(T)$ from the bulk binding energy thermal shift, which can be put in linear relation with the thermal expansion of the solid [14,15] and, hence, with the specific heat [16]. In this case, as well, we find a very good agreement with standard calorimetric measurements [Fig. 3(a), open triangles].

We have shown that, in the bulk case, our photoemission approach gives quantitative values of $U(T)$. Now, the question is whether we can use in a similar way the surface core-level data to obtain the surface internal energy, whose contribution is not recognizable macroscopically using standard calorimetric techniques because of the negligible value of the ratio of surface to bulk atoms.

For a two-dimensional array of atoms (surface), the phonon contribution to the internal energy *per* mole, within the Debye model is [13]

$$U_S(T) = 4R\frac{T^3}{(\theta_D^{(S)})^2}\int_0^{\theta_D^{(S)}/T} dx\,\frac{x^2}{e^x - 1}. \tag{4}$$

Here $\theta_D^{(S)}$is the surface Debye temperature.

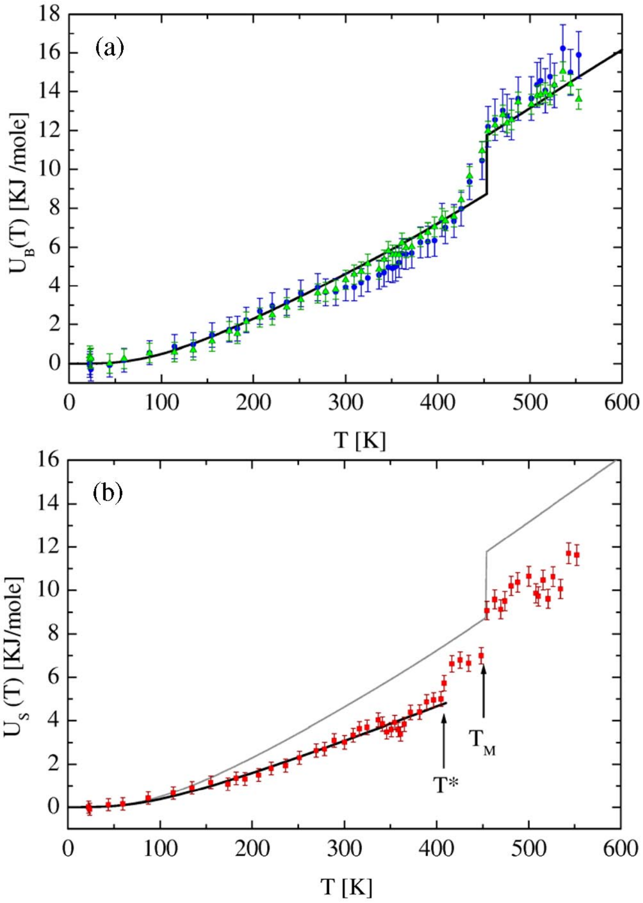

FIG. 3 (color online). Upper Panel: (a) Bulk internal energy as measured *via* calorimetry (solid line) [1], as obtained from phonon broadening (dots) and binding energy shift (open triangles) of the bulk component in our temperature-dependent photoemission data. Lower Panel: (b) Surface internal energy obtained from the phonon broadening of the surface peak (squares) using Eq. (6). The solid line is the theoretical surface internal energy, calculated with Eq. (4). For comparison the bulk internal energy as measured *via* calorimetry is also shown (thin gray line). The internal energy value at $T = 0$ has been subtracted for the sake of comparison.

Following the work of Hedin and Rosengren [8], it is possible to extend Eq. (1) to the core-level phonon broadening of the *surface atoms*, keeping in mind that we are now dealing with the phonon density of states in a two-dimensional lattice. The temperature dependence of the core-level linewidth can be written as

$$W_S^2(T) = W_{0S}^2\left[1 + c_S\left(\frac{T}{\theta_D^{(S)}}\right)^3\int_0^{\theta_D^{(S)}/T} dx\,\frac{x^2}{e^x - 1}\right] \tag{5}$$

with $c_S$ to be determined experimentally.

Fitting Eq. (5) to the surface data shown in Fig. 1, we obtained $c_S = 6 \pm 1$, $\theta_D^{(S)} = 415 \pm 20$ K, and $W_{0S}^2 = 0.152 \pm 0.006$ eV$^2$. The surface Debye temperature is in agreement with the value extrapolated from the surface phonon spectrum [17].

The relation between the internal energy and the phonon contribution to the core-level linewidth becomes

$$U(T) = -\frac{4R}{6}\theta_D^{(S)} + \frac{4R}{6}\frac{\theta_D^{(S)}}{W_{0S}^2}W_S^2(T). \qquad (6)$$

In Fig. 3(b) we show the surface internal energy obtained when substituting our experimental data in Eq. (6) (squares), superimposed to the surface internal energy calculated according to Eq. (4) (solid line). For comparison, the bulk $U(T)$ as measured via standard calorimetric techniques is also displayed (thin gray line) [1]. The two evident discontinuities in $U_S(T)$ correspond to temperature driven phase transitions. As already noted, the transition at 453 K corresponds to the bulk melting and the observed discontinuity ( $\sim 2.5$ kJ/mole), due to the latent heat at the transition, agrees with bulk measurements, confirming that Eq. (6) gives a quantitative estimation of $U_S(T)$.

The jump occurring at 404 K can be observed only in the surface data; it corresponds, therefore, to a surface phase transition. Being a first-order singularity and considering that the latent heat released ( $\sim 1.8$ kJ/mole) scales as the (bulk value)$^{2/3}$, we associate this phase transition to surface melting.

Surface melting is a critical phenomenon that may occur on low-index surfaces of metals [2,18,19]. It has been predicted and observed in fcc crystals on the most open (110) surface, but never in packed (111) surfaces [18–24]. In bcc crystals, like lithium at high temperature, the packing is reversed: The (110) surface is the most packed, even though the packing is looser than for the (111) surface of fcc crystals. Our work represents the first experimental observation of surface melting on a bcc crystal. The only available calculations on bcc crystals, at present, predict surface melting of $V(110)$ [25], and of alkali metal clusters [26].

Surface critical phenomena may be studied by low energy electron diffraction, which is the technique of choice to obtain the order of the phase transition and the critical exponent [27], but long-range order is needed. The present methodology based on high-resolution core-level photoemission has the unique characteristic to quantitatively measure the internal energy of surface atoms and does not necessarily require long-range order. It can be extended to any two-dimensional ordered or disordered array of atoms and molecules (for example organic monolayers) adsorbed on substrates or, more specifically, to nanostructures with large surface/bulk ratio (like nanotubes and nanodots), which play a fundamental role in nanotechnological applications, and which may not be studied by low energy electron diffraction .

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