Strong Energy Dependence of the Electron-Phonon Coupling Strength on Bi(100)

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We have studied the energy dependence of the electron-phonon coupling strength on Bi(100). A fit of the temperature-dependent surface state linewidth results in a change of the coupling parameter λ from 0.20 ± 0.02 to 0.72 ± 0.05 as the binding energy of the surface state increases from 70 to 330 meV. This result cannot be reconciled with the usual interpretation of λ as the electron-phonon mass enhancement parameter at the Fermi energy. We suggest that this behavior is mainly caused by the strong energy dependence of the bulk density of states in this region.

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The electron-phonon coupling is a many-body effect with considerable impact on the macroscopic properties of metals. It leads to a renormalization of the electronic band dispersion near the Fermi level and thereby changes the effective mass of the quasiparticles by a factor of $1 + \lambda$, where λ is the so-called electron-phonon mass enhancement parameter. This renormalization has a direct influence on properties such as the heat capacity or the resistivity. The electron-phonon interaction also provides the coupling mechanism in conventional superconductivity [1].

For three-dimensional systems, information on the detailed influence of the electron-phonon interaction on the self-energy can only be gathered indirectly. For surface states and two-dimensional systems such as the layered high-temperature superconductors, however, angle-resolved photoemission (ARPES) can be used for a detailed study of both the real and the imaginary part of the self-energy as a function of the wave vector, the binding energy, and the temperature. Two methods are used to determine λ from ARPES data. The first is to obtain λ from a fit to the temperature-dependent linewidth of a surface state [2]. The second is to use the renormalization of the quasiparticle dispersion near the Fermi level [3]. Both methods have different advantages but usually involve fitting to similar models and should be expected to give the same result at the Fermi level.

The study of the electron-phonon coupling with ARPES has led to some unexpected and confusing results. In an early investigation of the temperature-dependent linewidth of the Be(0001) surface state, for example, λ was found to have a value of 1.15 ± 0.1, much higher than the bulk value of 0.24 [4]. This gave rise to speculations about the possibility of surface-localized superconductivity. Later, however, it was acknowledged that this was partly due to a technical error in the analysis, and a determination of λ from the renormalized dispersion near the Fermi level yielded $\lambda = 0.7 \pm 0.1$ [5]. A similar experiment by a different group, on the other hand, reported a value of $\lambda = 1.18 \pm 0.07$ [6].

Some of these apparently contradicting results are due to purely technical difficulties in both strategies to determine λ. There are also sources of systematic error. One is that the λ value can depend dramatically on the position of $k_{\parallel}$ on the Fermi surface, as recently shown for another system [7], or perhaps also on the binding energy [8,9]. In this Letter, we show that λ can indeed depend strongly upon the binding energy of a state, a fact which raises fundamental questions about the meaning of λ determined from temperature-dependent linewidth data. We interpret this strong energy dependence as being due to the semimetallic character of our sample, Bi(100), and argue that this effect should be of high importance for systems with pronounced structure in the density of states, e.g., semimetals, molecular crystals, and narrow-band systems.

The surfaces of bismuth are interesting systems for studying the electron-phonon interaction. For amorphous Bi λ is 2.46 [10] but for single crystals it is quite small (see below). This can be explained by the very low density of states at the Fermi level of Bi in the rhombohedral crystal structure. The Bi(110) [11] and Bi(111) [12–14] surfaces have been found to support metallic surface states which turn them into better metals than the bulk; hence, a somewhat higher value of λ can be expected. We use the pseudohexagonal Bi(100) surface for the experiments described here. Its geometric and electronic structure are quite similar to that of the truly hexagonal Bi(111) surface. A detailed description of the electronic structure will be published elsewhere [15].

The surface was cleaned by cycles of Ne ion bombardment and annealing to 473 K. This resulted in a surface which was well ordered and clean as judged by low energy electron diffraction and Auger electron spectroscopy, respectively. Angle-resolved photoemission experiments were performed at the SGM-3 beam line of the synchrotron radiation source ASTRID in Aarhus [16]. The total energy resolution for the data shown below is 35 meV. The angular resolution of the analyzer is ±0.7°. The sample was cooled to approximately 30 K with a closed-cycle He

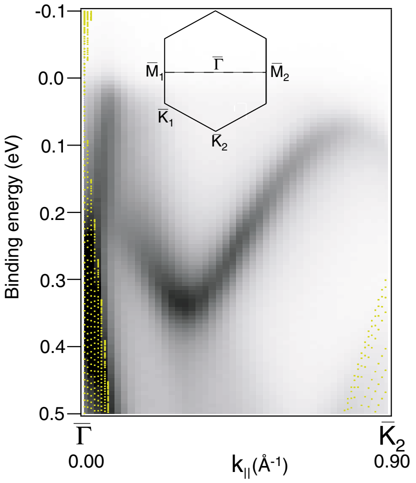

FIG. 1 (color online). Photoemission intensity as a function of binding energy and $k_{\|}$ in the $\bar{\Gamma}-\bar{K}_2$ direction of Bi(100). The photon energy was 19 eV. Dark corresponds to high photoemission intensity. The small dots are the result of a bulk band structure projection using the tight-binding parameters of Liu and Allen [17]. The inset shows the surface Brillouin zone. The mirror line, the only nontrivial symmetry element, is indicated as a dashed line.

cryostat. Measurements at higher temperatures were performed by heating the sample with the radiation from a filament mounted behind it.

Figure 1 shows the electronic structure of Bi(100) along the $\bar{\Gamma}-\bar{K}_2$ line together with a sketch of the surface Brillouin zone. Two genuine surface states are observed. One gives rise to a Fermi level crossing very close to $\bar{\Gamma}$, similar to the situation on Bi(111). The other one shows a relative maximum in binding energy at 330 meV and a relative minimum at 70 meV. By performing temperature-dependent measurements of the linewidth on many points of this surface state dispersion, we can extract the strength of the electron-phonon coupling at each point. Figure 2 shows such data sets for the two extrema of the dispersion. A mere visual inspection clearly shows that the temperature-induced broadening is much stronger at high binding energies. The figure also shows how the spectra were fitted. This was done by a Lorentzian line, a linear background, and a Fermi edge for the low binding energy spectra. The energy resolution of the experiment is irrelevant because it is always much better than the total linewidth.

In the following, we endeavor to determine the initial state linewidth Γ_i as a function of the temperature from the measured linewidth Γ_m. For surface states these are related by

$$\Gamma_m = \frac{\Gamma_i}{\left|1 - \frac{m v_{i\|} \sin^2\theta}{\hbar k_{\|}}\right|}, \qquad (1)$$

where $v_{i\|}$ is the group velocity of the initial state and θ the off-normal emission angle [18]. For the two extrema

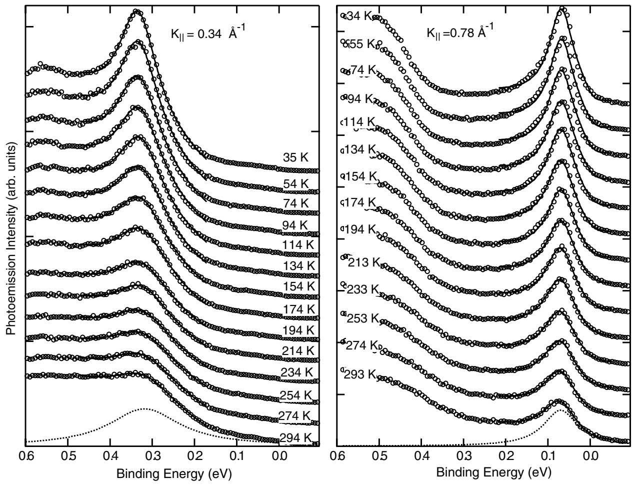

FIG. 2. Temperature dependence of the surface state for different binding energies taken at $h\nu = 19$ eV. The solid lines are the result of a peak fit, as described in the text.

in the dispersion, the group velocity is zero and Eq. (1) reduces to $\Gamma_m = \Gamma_i$. For the remaining points, the initial state linewidth has to be calculated but the correction is very small because of the small overall group velocity and because we are rather close to normal emission. Another issue which has to be addressed is the finite angular acceptance of the electron analyzer which could lead to a distortion of the peaks, in particular, when probing a steeper part of the dispersion. We have numerically simulated this effect for the present situation and found it to be negligible.

Figure 3 shows the resulting initial state linewidth as a function of temperature for four points. These data were fitted with the calculated electron-phonon contribution to the lifetime [2]. The phonon spectrum was represented in the bulk Debye model with a Debye temperature of 50 K, guided by the value for Bi(111) [19]. The actual fit is the sum of the temperature-dependent electron-phonon contribution to the lifetime plus a temperature-independent offset Γ_0. Such an analysis is based on the assumption that the temperature dependence due to the electron-phonon contribution is much larger than that of the other decay mechanisms, i.e., Auger decay and defect scattering. Formally, Γ_0 would be containing only the contribution of these latter two mechanisms, but in practice it can also be influenced by the background of the spectra. In order to test this, we have performed many similar scans at different photon energies and at equivalent $k_{\|}$ points in different surface Brillouin zones. We can conclude that Γ_0 can change as a function of these parameters but the value of λ is robust. Note that our fit is not merely a linear interpolation but a fit to the full Debye model. Because of the low Debye temperature, however, the result of the fit is approximately linear.

From many such data sets, we eventually get the final result, λ as a function of binding energy and/or $k_{\|}$. This is

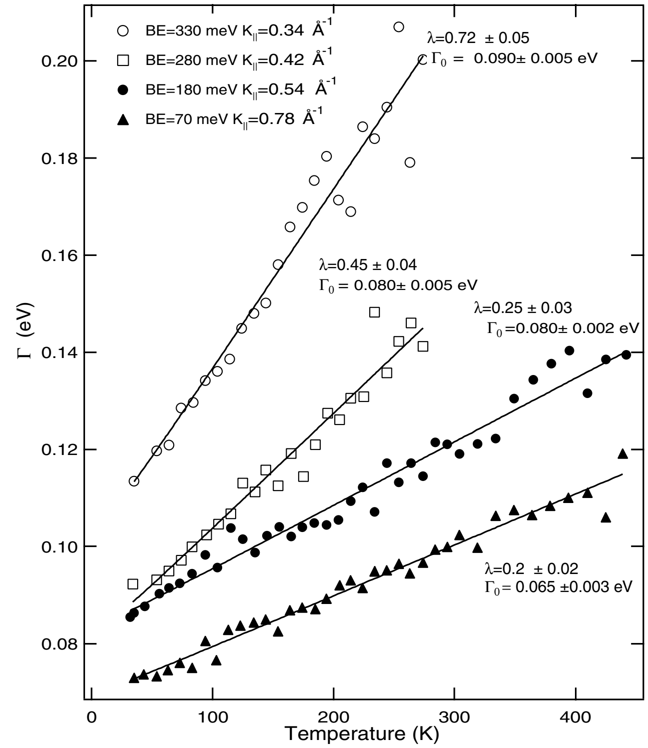

FIG. 3. Temperature-dependent linewidth of the surface state for four different binding energies (BE) and fit to the data within the Debye model (see text).

given in Fig. 4. It is clearly seen that λ depends strongly on the binding energy of the state. Moreover, the data points on the low binding energy side show an additional $k_{||}$ dependence because we get different values of λ on both sides of the binding energy minimum shown in Fig. 1. It is obvious from this plot that an interpretation of λ as a mass enhancement parameter at the Fermi energy is not meaningful here. It is more appropriate to view λ as a value indicating the electron-phonon coupling strength at a certain binding energy and $k_{||}$.

There are several ingredients which can cause the strong energy dependence of λ demonstrated in Fig. 4 and the best possible approach to an interpretation would be a comparison to a calculated lifetime broadening such that the individual contributions can be extracted. This has recently been demonstrated convincingly for the surface states of Cu(111) and Ag(111) [20]. In the case of Bi, however, such a calculation would be very difficult. Instead, we suggest that the main reason for the behavior described above lies in the semimetallic nature of Bi. λ is related to the Eliashberg coupling function α^2F by [1]

$$\lambda = 2\int_0^{\omega_m} d\omega'\, \alpha^2F(\omega')/\omega', \tag{2}$$

where ω_m is the highest phonon energy and α^2F can be written as [20,21]

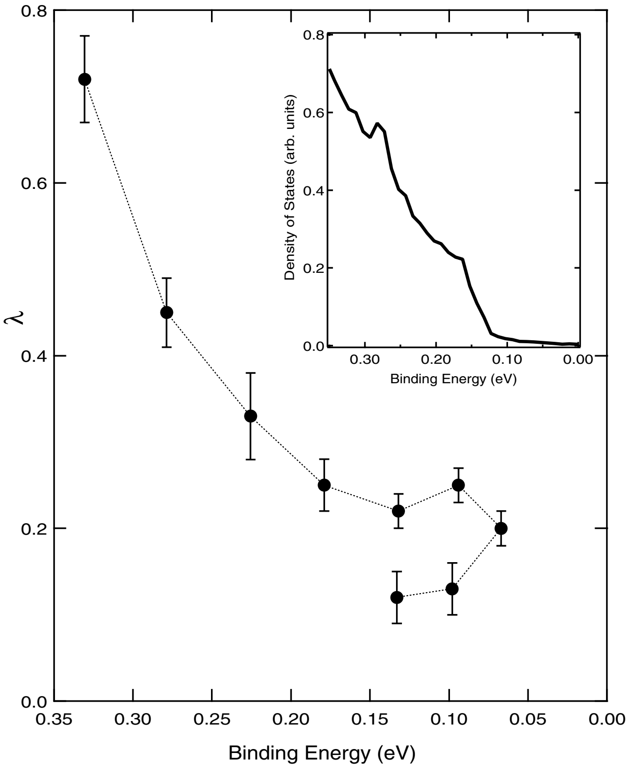

FIG. 4. Electron-phonon coupling parameter λ as a function of binding energy. The dotted line between the data points connects the points as they lie on the $\bar{\Gamma} - \bar{K}_2$ line. The inset shows the bulk density of states of Bi as a function of binding energy as calculated using the tight-binding parameters from Liu and Allen [17].

$$\alpha^2F_{\vec{k}_i}(\omega) = \sum_{\vec{q},\nu,f} |g_{i,f}^{\vec{q},\nu}|^2\, \delta(\omega - \omega_{\vec{q},\nu})\, \delta(\epsilon_{\vec{k}_i} - \epsilon_{\vec{k}_f}), \tag{3}$$

which, if we assume a constant matrix element $g_{i,f}$, is simply a sum over the different possibilities to fill a hole state with an electron using a phonon to provide energy and momentum. For Bi, the total width of the phonon spectrum is very small; the maximum (bulk) phonon energy is 13.8 meV [22]. Therefore an energy dependence of α^2F will mainly be given by the electronic density of available states (DOS). The bulk DOS is known to vary dramatically in the vicinity of the Fermi energy, as shown in the inset of Fig. 4. Our interpretation of the data is that the λ we have found basically mimics this bulk density of states. This is supported by the apparent similarity of the DOS and the trend observed in λ. However, we totally neglect any contribution from the surface states which turn this Bi surface into a substantially better metal than the bulk, similar to the cases of Bi(110) and Bi(111) [11–14]. We believe this to be justified because it is inconceivable that the surface density of states has a similar dramatic energy dependence as the bulk DOS. We also neglect the energy dependence of the matrix element, and it is clear that our simple approach emphasizes only one aspect of a complex problem. Other factors could also play a role. It has been suggested that an energy or $k_{\|}$ dependent separation of the surface state band from the bulk continuum leads to a different localization of the surface state and therefore also to a different λ [8]. It is obvious that for a more detailed interpretation calculations similar to those in Refs. [20,21] will be necessary.

In light of this interpretation, it seems sensible to ask what the value of the electron-phonon coupling parameter λ at the Fermi energy in crystalline bulk Bi actually is. To the best of our knowledge, no such value is given in the literature. We can make a simple estimate by considering the renormalization of the low temperature heat capacity. We can estimate the expected heat capacity from the unrenormalized density of states which we obtain using the tight-binding parameters given by Liu and Allen [17] and compare this value to the measured heat capacity [23]. From this we get $\lambda = 0.13(-0.13 + 0.2)$. This small value is consistent with the data presented above, and our explanation for the behavior, which is based on the DOS argument, is also consistent with the high λ observed for amorphous Bi.

The consequences of our work reach far beyond this specific system. A determination of λ by fitting the temperature-dependent peak width has several practical advantages over the determination from the band renormalization near a Fermi level crossing. One is the uncertainty in the latter approach when the phonon energy scale or the coupling is small or when the unrenormalized dispersion is not known. Another is that there are systems which show metallic behavior but have thus far not revealed any clear quasiparticle states crossing the Fermi level, e.g., some fullerite compounds and some transition metal oxides. In fact, numerous determinations of λ based on the temperature-dependent linewidth of surface states have been published. However, our results clearly show that λ determined by this approach cannot be identified with the mass enhancement parameter at the Fermi energy, the quantity of most relevance. One should at least try to measure the temperature-dependent linewidth for states very close to the Fermi energy, or one could attempt to normalize the λ obtained at a finite energy by the ratio of the DOS at this energy and that at the Fermi energy.

In conclusion, we have shown that the electron-phonon coupling strength varies strongly as a function of binding energy on Bi(100). We suggest that this is mainly related to the change of the bulk density of states in the region of interest. Taking DOS-induced changes of λ into account is essential if one tries to estimate the strength of the electron-phonon coupling at the Fermi level from the temperature dependence of higher binding energy states. Such corrections should be particularly important for systems which show pronounced DOS variations, such as semimetals, molecular crystals, or narrow-band systems. Moreover, even a small energy dependence of the electron-phonon coupling at higher binding energies might be important when more subtle details are to be extracted from the spectral function, in particular, in the case of high-temperature superconductors [24].

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[1] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981).
[2] B. A. McDougall, T. Balasubramanian, and E. Jensen, Phys. Rev. B **51**, 13 891 (1995).
[3] T. Valla, A.V. Fedorov, P. D. Johnson, and S. L. Hulbert, Phys. Rev. Lett. **83**, 2085 (1999).
[4] T. Balasubramanian, E. Jensen, X. L. Wu, and S. L. Hulbert, Phys. Rev. B **57**, R6866 (1998).
[5] S. LaShell, E. Jensen, and T. Balasubramanian, Phys. Rev. B **61**, 2371 (2000).
[6] M. Hengsberger, D. Purdie, P. Segovia, M. Garnier, and Y. Baer, Phys. Rev. Lett. **83**, 592 (1999).
[7] E. Rotenberg and S. D. Kevan, J. Electron Spectrosc. Relat. Phenom. **126**, 125 (2002).
[8] E. Rotenberg, J. Schaefer, and S. D. Kevan, Phys. Rev. Lett. **84**, 2925 (2000).
[9] D.-A. Luh, T. Miller, J. J. Paggel, and T.-C. Chiang, Phys. Rev. Lett. **88**, 256802 (2002).
[10] T.T. Chen, J.D. Leslie, and H.J.T. Smith, Physica (Amsterdam) **55**, 439 (1971).
[11] S. Agergaard, C. Søndergaard, H. Li, M. B. Nielsen, S.V. Hoffmann, Z. Li, and P. Hofmann, New J. Phys. **3**, 15.1 (2001).
[12] M. Hengsberger, P. Segovia, M. Garnier, D. Purdie, and Y. Baer, Eur. Phys. J. B **17**, 603 (2000).
[13] Ch. R. Ast and H. Höchst, Phys. Rev. Lett. **87**, 177602 (2001).
[14] Ch. R. Ast and H. Höchst, Phys. Rev. B **66**, 125103 (2002).
[15] J. E. Gayone *et al.* (unpublished).
[16] S.V. Hoffmann, C. Søndergaard, C. Schultz, Z. Li, and Ph. Hofmann (to be published).
[17] Y. Liu and E. Allen, Phys. Rev. B **52**, 1566 (1995).
[18] N.V. Smith, P. Thiry, and Y. Petroff, Phys. Rev. B **47**, 15 476 (1993).
[19] R. M. Goodman and G. A. Somorjai, J. Chem. Phys. **52**, 6325 (1970).
[20] A. Eiguren, B. Hellsing, F. Reinert, G. Nicolay, E.V. Chulkov, V. M. Silkin, S. Hüfner, and P. M. Echenique, Phys. Rev. Lett. **88**, 066805 (2002).
[21] B. Hellsing, A. Eiguren, and E.V. Chulkov, J. Phys. Condens. Matter **14**, 5959 (2002).
[22] J. L. Yarnell, J. L. Warren, R. G. Wenzel, and S. H. Koenig, IBM J. Res. Dev. **8**, 234 (1964).
[23] H. K. Collan, M. Krusius, and G. R. Pickett, Phys. Rev. B **1**, 2888 (1970).
[24] A. Damascelli, Z. Hussain, and Z.-X. Shen, Rev. Mod. Phys. **75**, 473 (2003), and references therein.