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Large value of the electron-phonon coupling parameter ($\lambda = 1.15$) and the possibility of surface superconductivity at the Be(0001) surface

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The electron-phonon coupling parameter λ_s at the Be(0001) surface is measured using angle-resolved photoemission and found to be 1.15 ± 0.1, more than four times the bulk Be value $\lambda_b = 0.24$. This large value for λ_s may imply the existence of an unusual form of surface superconductivity with a correspondingly large transition temperature. [S0163-1829(98)50312-8]

The electronic density of states (DOS) at the Fermi level (E_F) at the Be(0001) surface is about four times larger than in the bulk.[1] The E_F DOS is an important parameter for describing many electronic processes. Anomalously large surface core-level shifts[1,2] and giant surface Friedel oscillations[3] have been observed on this surface, and have been attributed to the large surface to bulk E_F DOS ratio. Electron-phonon coupling should also be enhanced. In a typical electron-phonon interaction event, an electron scatters from one state to another with the emission or absorption of a phonon. By simple Fermi golden rule arguments, one expects the probability for this interaction to be proportional to the density of states into which the electron can scatter. Since phonon and thermal energies are small on the scale of electronic energies and the final-state energy is near to E_F, the coupling should be proportional to the electronic density of states at E_F. The strength of the electron-phonon interaction is conventionally measured by the dimensionless parameter λ, called the mass enhancement or coupling parameter. Accordingly, λ_s at the Be(0001) surface should be near unity, four times larger than the bulk value $\lambda_b = 0.24$.[4] Since the interaction also depends on the phonon spectrum and the strength of the scattering matrix elements, which are potentially different at the surface than in the bulk, an experiment is necessary to determine whether λ_s is in fact as large as this estimate. We find that $\lambda_s = 1.15$, more than four times larger than λ_b.

Many properties of solids depend directly on λ. These include resistivity, superconductivity, structural instabilities, the specific heat, and the shape of the one-electron bands for energies near the debye energy. Of particular interest is the possibility that a large λ_s can lead to surface superconductivity at temperatures well above the bulk Be superconducting transition temperature (T_c) of 0.026 K.[5] A naive application of the standard formula that connects λ to T_c yields 70 K for the Be(0001) surface.[4] This formula is known to be inapplicable to thin superconducting films on nonsuperconducting substrates due to the proximity effect.[6] We propose a form of surface superconductivity where only the surface states pair. This system should have a high T_c potentially as high as 70 K.

It has been shown that angle-resolved photoemission (ARP) can be used to determine λ_s for crystalline metal surfaces.[7] The basic idea is that, under proper conditions, the observed width of a surface-state peak is equal to $\hbar/\tau$, where τ is the lifetime of the surface-state hole excitation. Since virtually all of the temperature dependence of τ is in the phonon contribution, a measurement of the temperature dependence of the surface-state width is effectively a measurement of the temperature dependence of the phonon contribution to the hole lifetime. At high temperatures and small hole energies the temperature dependence of the phonon contribution to the inverse hole lifetime is given by $\hbar/\tau = 2\pi\lambda kT$.[4] In this limit, λ is just $2\pi k$ times the slope of the peak width vs temperature curve, and is easily measured. More careful consideration shows that this high temperature limit is approximately valid for temperatures greater than about one-third the debye temperature, and for hole energies small compared to the bandwidth.[4] The depth beneath the surface over which λ_s is averaged in this technique is determined by the penetration depth of the surface state, which is a few atomic layers for most surface states.

We study a state on the Be(0001) surface that exists in a wide region of momentum space centered on the zone center $\bar{\Gamma}$.[8] It disperses parabolically from a maximum binding energy of 2.78 eV at $\bar{\Gamma}$, and crosses E_f at a momentum $k_F = 0.95\ \text{Å}^{-1}$, about halfway to the Brillouin-zone boundary $\bar{K}$ at $1.84\ \text{Å}^{-1}$. This corresponds to an effective mass of $1.17 m_e$. At room temperature we observe a width of 0.40 eV at $\bar{\Gamma}$, which reduces to about 0.32 eV at a binding energy of 0.35 eV. These observed widths are a combination of contributions from the electron-phonon, electron-electron, and electron-impurity interactions.

The data were taken on the U12 beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. The ARP analyzer is a 50-mm mean radius hemispherical analyzer. A Be single crystal was cut and mechanically polished to within 0.25° of (0001) by the Materials Preparation Center of Ames Laboratory. The sample was electropolished before mounting in the chamber. The sample was mounted on 0.010-in-diam tungsten wires. Our initial cleaning procedure consisted of sputtering both the front and back of the

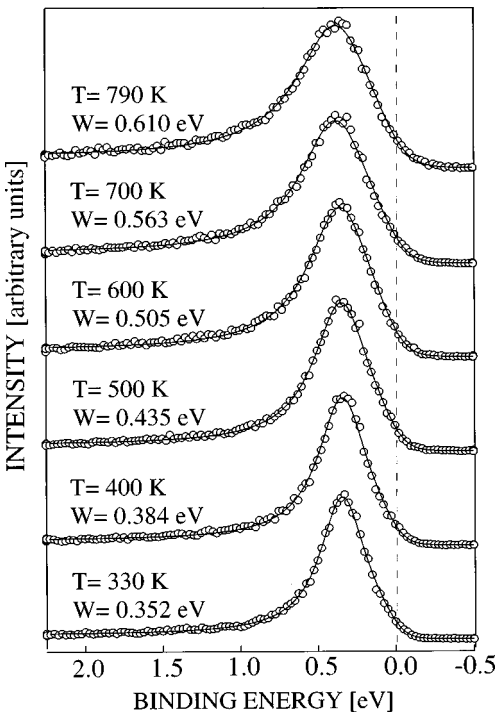

FIG. 1. Surface-state spectra at several temperatures. The momentum is 0.89 Å^{-1}, the hole energy is 0.35 eV, and the photon energy is 15 eV. The open circles are the experimental data. Typically there are 1500 counts in the peak. The line is a fit to a function of the form Lorentzian plus constant times the Fermi distribution. Temperatures (T) and widths (W) derived from the fit are as indicated.

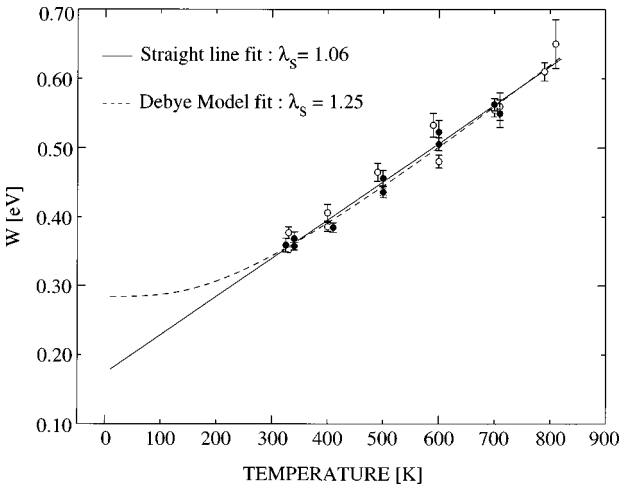

FIG. 2. Surface-state widths from fits like those shown in Fig. 1 vs temperature. These data include two full cycles from room temperature to 800 K and back to room temperature. The error bars on the data are statistical uncertainties from the fits. The open circles are for increasing temperature and the filled circles are for decreasing temperature.

sample for several hours with 2-keV Ne ions to remove the initial oxide layer. Subsequently, cleaning consisted of sputtering at 1 keV and annealing to 450–600 °C. During data acquisition, the heating current was pulsed at 1 kHz with a duty cycle of 20% and electron counting was disabled during the heating pulse. All data presented were taken at $\hbar\omega = 15$ eV. The light was incident s polarized at 30° from the sample normal in the vertical plane. The electron exit angle was 33° in the horizontal plane, corresponding to $k_{\parallel} = 0.89\ \text{Å}^{-1}$ in the Γ-K direction, with a binding energy of 0.35 eV. The angular resolution was 10×10 mR, corresponding to $\Delta k_{\parallel} = 0.013\ \text{Å}^{-1}$. The total energy resolution was 0.2 eV. The peak count rates were near 100 Hz.

In Fig. 1 we show spectra and fits vs temperature. The fits are to the function Lorentzian plus constant multiplied by a Fermi function. The constant background is a crude approximation to the true inelastic background, but the background is such a small part of the spectrum that this form is adequate, and preferred for simplicity. It is clear from the quality of the fits that the peaks are Lorentzian, indicating that the interpretation of the widths as inverse lifetimes is valid. The strong temperature dependence of the widths is also clear from the raw data.

The widths derived from these and other fits are plotted vs temperature in Fig. 2. The fit of these widths to a straight line is shown; the slope yields $\lambda_s = 1.06$. The debye temperature of Be is quite large (the bulk value is near 1000 K (Ref. 9)) and the straight-line fit is only approximately valid in the temperature range of our data. One can fit directly to the more general equation $\hbar/\tau(\omega,T) = 2\pi\hbar\int_0^{\omega_m} d\omega'\,\alpha^2F(\omega')[1 - f(\omega-\omega') + 2n(\omega') + f(\omega+\omega')]$ if one assumes a model for the Eliashberg coupling function $\alpha^2F(\omega)$; n and f are the Bose and Fermi distribution functions.[4] We use a debye model [$\alpha^2F(\omega) = \lambda\omega^2/\omega_D^2$ and $\omega_m = \omega_D$], and the bulk debye temperature of 1000 K. This fit yields $\lambda_s = 1.25$. We choose to interpret these two values for λ_s (1.06 and 1.25) as typical of the range of values that could result from the analysis, and quote 1.15 ± 0.1 as the measured value. ω_D of the surface could, in principle, be quite different than that of the bulk. A recent analysis of the surface phonon dispersion shows, however, that there are surface phonons with energies near 70 meV, and calculations show that the highest energies are near 80 meV corresponding to ω_D near that of the bulk.[10] In principle, ω_D could be derived from a fit to the data, but lower temperature data would be required for such an analysis to be useful.

It is common for large values of λ to be associated with high T_c's, especially in materials such as Be with large ω_D. For a homogeneous system,[11] T_c can be found from the following formula:[4] $kT_c = (\hbar\omega_D/1.45)e^{-1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)]}$. μ^* represents the effective Coulomb interaction and is typically 0.1. For bulk Be $\lambda_b = 0.24$; $\mu^* = 0.1$, and the debye temperature $T_d = 1000$ K, resulting in $T_c = 0.024$ K; this compares well with the measured value of 0.026 K.[5] If we use the surface value $\lambda_s = 1.15$ and leave the other parameters unchanged, we obtain $T_c = 70$ K. This is incorrect, as it ignores the well-known suppression of T_c for a thin film on a nonsuperconducting substrate. The missing physics is that Cooper pairs formed in the surface region where the interaction is high can leak into the bulk and break apart. This effect has been quantified by De Gennes,[6] and essentially no enhancement is expected if we think of our surface as a few Å film with large λ on a thick bulk substrate with low λ. If, however, a thin film with the (0001) structure could be grown on an insulating substrate, it ought to exhibit a high T_c. It is well known that

amorphous thin films of Be have T_c near 10 K.[12] It is thought that the different structure enhances the DOS at E_F, increasing λ and T_c as above.

The most interesting possibility that we have considered is that the surface states superconduct without direct involvement of the bulk states: Cooper pairs would be formed between surface-state levels $(k_\parallel\uparrow, -k_\parallel\downarrow)$, while bulk states would remain normal. Since electrons in surface states are trapped at the surface and cannot leak into the bulk, the mechanism discussed above for breaking up pairs does not apply. This system can be described by the two band model, solved within the Bardeen-Cooper-Schrieffer (BCS) formalism by Suhl, Matthias, and Walker[13] in 1959. This model was intended to represent *s* and *d* electrons in transition metals, but the formalism is the same for any system characterized by two distinct branches of the Fermi surface, which includes surface and bulk states. Each branch i has its own λ_{ii}, and there is coupling between the branches given by λ_{ij} and λ_{ji}. For simplicity, we specialize to the case where there is no bulk interaction $(\lambda_{BB}=0)$. The superconducting transition is characterized by a formula identical in form to the BCS formula for a single band, $kT_c=1.14\hbar\omega_D e^{-1/\lambda_{\rm eff}}$, where $\lambda_{\rm eff}=\frac{1}{2}(\lambda_{SS}+\sqrt{\lambda_{SS}^2+4\lambda_{SB}\lambda_{BS}})$. In the limit of a thick crystal λ_{BS} is negligible,[14] and $\lambda_{\rm eff}=\lambda_{SS}$. The surface-state electrons pair, with gap and transition temperature the same as they would be for an isolated surface-state system, and the bulk electrons remain normal. Since only λ_{SS} appears in the formulas describing pairing, while both λ_{SS} and λ_{SB} play a role in the decay of surface-state holes, the $\lambda_{\rm eff}$ relevant to pairing will be lower than $\lambda_s=1.15$ determined by the decay rate. This should be a small effect, as most of the E_F DOS at the surface is from surface states, and thus most of the decay of surface states is to other surface states. A transition temperature near 70 K and a zero temperature gap $(2\Delta_0)$ near 20 meV seem reasonable expectations.

Impurities/defects will likely play a more important role in destabilizing this system than they do in homogeneous superconductors. The problem is that the impurities scatter surface states into bulk states, the one-electron eigenstates become linear combinations of surface and bulk states, and the pairing interaction is averaged over surface and bulk. Since the interaction in the bulk is weak, any averaging will quickly destroy superconductivity at the surface. It is known that two band effects are destroyed if the mean free path is shorter than the superconducting coherence length.[15] The zero temperature coherence length of a superconductor can be written as $\xi_0=\hbar v_F/(2\pi_k T_c)$, where v_F is the Fermi velocity. For the Be(0001) surface, assuming a 70 K T_c, ξ_0 is about 300 Å. A mean free path as large as this is difficult to achieve on a metal surface. However, only the interband (surface to bulk) scattering should contribute to the averaging. Since the surface-state DOS is much larger than the bulk-state DOS, surface to surface scattering should be much more common than surface to bulk scattering, and a much smaller mean free path may be adequate. Be(1010), with a similarly large surface to bulk E_F DOS ratio as Be(0001), and a much smaller v_F may be a better candidate to observe the phenomenon of surface-state superconductivity.[16]

If the surface states do pair at elevated temperatures, they represent an interesting opportunity to study two-dimensional superconductivity for a simple system with a relatively large energy scale. The one-electron origins of the many-body state are simple and well characterized (parabolic bands, nearly circular Fermi surface), and the pairing mechanism (phonons) is well understood. The superconducting energy gap ought to be resolvable by high-resolution ARP spectrometers and by scanning tunneling microscopes (the BCS value of Δ is 10 meV for a 70 K T_c). The critical current density j_c at zero temperature can be estimated by noting the maximum momentum a pair can have before it can decay by one-electron processes. In three dimensions this analysis yields $j_c=2ne\Delta/(\hbar k_F)$, where e is the electron charge, Δ is the gap, and n is the (super) electron density.[17] In two dimensions the analysis is identical, except n is a surface electron density and j_c is a surface current density. Using $\Delta=10$ meV, $\hbar k_F=0.95$ Å^{-1}, and $n=0.14/$Å^2, one finds $j_c=70$ A/cm.

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