Temperature Dependent Complex Band Structure and Electron-Phonon Coupling in Ag

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The band dispersion and lifetime width for the sp valence electrons in Ag are determined with unprecedented accuracy as a function of temperature. The resulting Fermi wave vector challenges the venerable de Haas–van Alphen value, and shows the latter to be off by 1%. The electron-phonon mass enhancement parameter is deduced for the first time for a bulk state, and it is significantly larger than theoretical estimates. These measurements are made by photoemission from quantum well states in atomically uniform films of Ag.

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The coupling of electrons and phonons is an important issue in solid state physics, since it is the origin of a variety of effects and a model case for quasiparticle interactions. A well-known phenomenon resulting from the electron-phonon coupling is the "classical" superconductivity as discussed by Bardeen, Cooper, and Schrieffer. Of central importance to this classical theory is the electron-phonon mass enhancement parameter λ [1,2], which characterizes the renormalization of electronic band mass due to electron-phonon coupling. This parameter has a directional anisotropy but usually only its average value is measured if an experimental value is known at all. In most cases, no reliable number for the mass enhancement parameter is available and only guesses can be made. Theoretically, it can be related to the temperature dependence of the imaginary part of the band structure (lifetime broadening) [1–3], and a measurement should be possible by angle-resolved photoemission [4]. In practice, the lifetime information is generally obscured by the much larger final-state damping effect and by extrinsic broadening mechanisms such as defect scattering [5]. As a result, no reliable measurements of λ are available for three-dimensional materials. There have been a few successful photoemission measurements for surface states, for which the final state damping effect is suppressed because of the reduced dimensionality [6,7]. However, such results are not necessarily relevant to the bulk properties because the surface states are energetically and spatially decoupled from the bulk.

Recent advances in the preparation of atomically uniform films [8] and in theoretical understanding of quantum well spectroscopy based on photoemission [9] have made accurate measurements of the complex band structure possible. This methodology is employed here for a study of the temperature dependence of the complex band structure of the Ag sp state. The imaginary part of the band structure, measured over a wide temperature range, yields a value for the electron-phonon mass enhancement parameter $\lambda = 0.29 \pm 0.05$ along [100], which is significantly larger than available theoretical estimates [1]. This finding may have significant impact on our understanding of the behavior of Ag as a commonly used contact material to superconductors [10]. An extrapolation of the real part of the Ag band structure to zero temperature yields a Fermi wave vector along the [100] direction $k_F/k_{\Gamma X} = 0.829 \pm 0.001$. This result is significantly more accurate than the value obtained by the de Haas–van Alphen method [11], which has been long regarded as the method of choice for Fermi surface measurements.

Our photoemission data were taken at the 4-m Normal Incidence Monochromator beam line of the Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, Wisconsin. The substrate was a Fe(100) whisker, onto which epitaxial Ag films were grown by deposition at low temperature followed by annealing. Additional Ag was added as needed to make the coverage equal to an exact integer multiple of a monolayer (ML). The resulting films were atomically smooth and stable against temperature cycling between 100 and 500 K. The absolute film thickness in terms of monolayers was determined by counting discrete quantum well peaks as a function of film thickness. Photoelectrons were detected with a small hemispherical analyzer. A normal emission geometry was employed.

As an example of our results, Fig. 1 shows a set of spectra taken from a 19-ML film at several temperatures as indicated. The width of the Fermi edge broadens as the temperature of the sample rises. The two peaks in each spectrum are derived from quantum well states, and correspond to standing electron waves within the Ag film. These standing waves are analogs to optical cavity modes in a Fabry-Pérot interferometer [12], and the curves in the figure are fits to the data (dots) using a generalized Fabry-Pérot formula [9]. As the temperature rises, the peak heights decrease (reduction in interferometer contrast), and the peaks widen and shift. The shifts are very small, but noticeable when the peak positions are compared to the vertical reference lines. The peak at higher binding

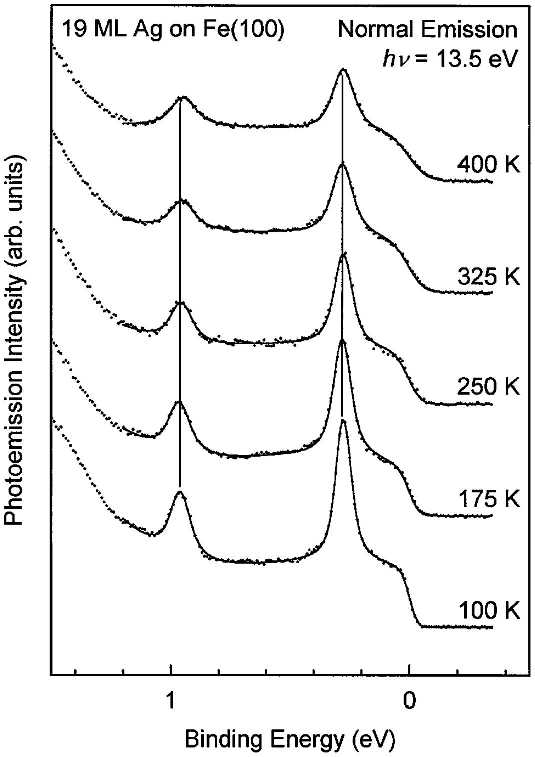

FIG. 1. Normal emission spectra (dots) from a 19 ML thick Ag film on Fe(100) taken at various temperatures. The curves represent a fit using a generalized Fabry-Pérot formula. The vertical reference lines highlight peak shifts.

energy shows a larger shift. Similar results have been obtained for other film thicknesses.

Based on the Fabry-Pérot model, the quantum-well peak width is determined by the quasiparticle inverse lifetime and the reflectivity at the interface. Since the reflectivity is tied to the band structure mismatch between Ag and Fe, this is not expected to change. The thermally induced peak broadening simply reflects an increase in lifetime broadening due to phonon scattering. The quasiparticle inverse lifetime is given by

$$w(E,T) = w_0 + w_1(T) + w_2 E^2, \qquad (1)$$

where E is the binding energy. The first term, being independent of T and E, represents the contribution from residual defect scattering. The second term depends on T and represents phonon scattering. The third term has an E^2 dependence, and represents electron-electron scattering in a Fermi liquid. Equation (1) implies that the E and T dependencies are decoupled. This is valid provided the binding energy is not too small (greater than about 50 meV) [7]. We include in our analysis only quantum well peaks satisfying this condition. From an earlier study carried out at a single temperature (100 K), $w_2 = 25.6\ \text{meV}/\text{eV}^2$ [9].

Quantum well data for 14 and 19 ML thicknesses are analyzed simultaneously using the generalized Fabry-Pérot formula to deduce the peak width w. The contribution from the electron-electron scattering term in Eq. (1) is then subtracted away to yield $w_0 + w_1(T)$. The results, independent of E, are shown in Fig. 2 as dots. The temperature dependence of $w_1(T)$ is given by

$$w_1(T) = 2\pi \int_0^{\omega_D} \lambda\left(\frac{\omega}{\omega_D}\right)^2 [1 - f(\omega - \omega') + 2b(\omega') + f(\omega + \omega')]\, d\omega', \qquad (2)$$

where the electron-phonon mass enhancement parameter λ enters as a proportionality constant, ω_D is the Debye frequency (0.0194 eV), and f and b are the Fermi-Dirac and Bose-Einstein distribution functions, respectively [1]. The solid curve in Fig. 2 is a fit, and the fitting parameters are $\lambda = 0.29 \pm 0.05$ and $w_0 = 8$ meV. The latter corresponds to a quasiparticle coherence length of about 1000 Å in the absence of phonon scattering and electron-electron scattering.

As far as we know, this is the only experimental determination of λ available for bulk Ag in the literature. Grimvall [1] and Allen [13] have given a theoretical estimate of $\lambda_{\text{ave}} = 0.13$ and 0.12, respectively, for λ averaged over the Fermi surface. These average values are much smaller than our measured value along the [100] direction. Although the directional anisotropy in Ag has not been calculated to the best of our knowledge, such calculations are available for Cu, another noble metal with a very similar Fermi surface topology and a very similar λ. The best theoretical estimate for Cu varies from $\lambda = 0.08$ in the [110] direction to $\lambda = 0.15$ in the [111] and [100] directions, yielding an average value essentially the same

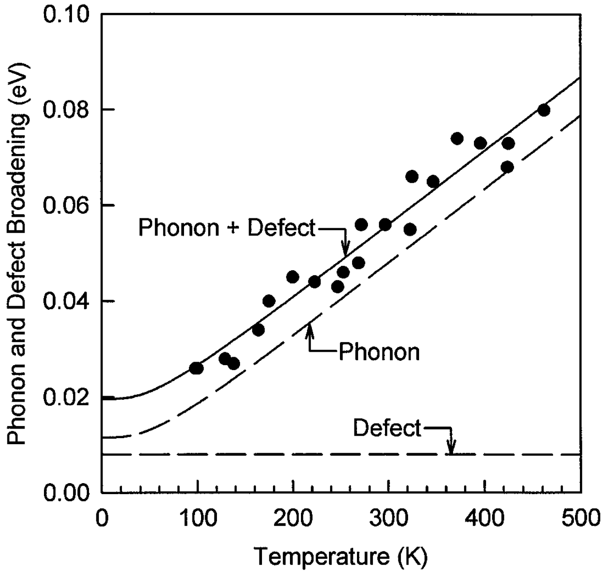

FIG. 2. The dots represent experimental results for the sum of phonon and defect scattering contributions to the quasiparticle inverse lifetime. The solid curve is a fit, and the dashed curves indicate the separate phonon and defect contributions. Note that the phonon contribution does not vanish at $T = 0$ because phonon emission is still possible.

as that for Ag [14]. Comparing our $\lambda_{100} = 0.29$ along [100] to the theoretical value of 0.15, there is almost a factor of 2 difference. The discrepancy is not surprising in view of the approximations made in those theoretical estimates. A cyclotron resonance measurement has suggested that $\lambda_{100} = 0.21$ for Cu [15]. This is closer to our measurements, but the accuracy of this method has been questioned [7]. Our results suggest that the best estimate of λ_{ave} for Ag is $0.12 \times (0.29/0.15) = 0.23$ obtained by simply scaling the theoretical average value by the ratio between our measured value along [100] and the corresponding theoretical value. It is interesting to note that $\lambda_{\text{ave}} = 0.24$, 0.37, 0.40, and 0.43 for Be, Zn, Cd, and Al, respectively [1], which are large enough to make these simple metals superconducting with transition temperatures of 0.03, 0.9, 0.6, and 1.2 K, respectively. Being nominally nonsuperconducting, Ag appears to be much closer to the borderline than previously thought.

The shifts of quantum well peaks as seen in Fig. 1 can be attributed to three possible causes: (1) thermal expansion of the Ag lattice resulting in a change in the interferometer path length, (2) temperature dependence of the band structure, and (3) a change in phase shift at the Ag-Fe boundary. The peak positions are determined by the Bohr-Sommerfeld quantization rule

$$2kNt + \Phi = 2n\pi\,, \tag{3}$$

where N is the number of monolayers in the film, t is the monolayer thickness, Φ is the sum of the surface and interface phase shifts, and n is a quantum number [9]. The thermal expansion coefficient of Ag is $19 \times 10^{-6}\ \mathrm{K}^{-1}$, and its effect on the interferometer thickness Nt can be calculated. The result is insufficient to describe the observed peak shift. A change in band structure is accompanied by a change in the wave vector k, which would cause peak shift, and so would a change in Φ. These two effects can be distinguished by the N (layer thickness) dependence. A change in k is amplified by a factor of N in the phase shift, while there is no such amplification for Φ. A careful analysis involving data for different film thicknesses shows that Φ does not change as a function of T. Thus, there must be a change in band structure.

The same Fabry-Pérot analysis, with the thermal expansion taken into account, yields the temperature dependence of the band structure. The results are summarized in Fig. 3. Figure 3(a) shows the occupied part of the Ag sp band at two temperatures 100 and 400 K. As the temperature rises, the Brillouin zone size changes due to a changing lattice constant. To avoid this complication, the horizontal axis in Fig. 3(a) is chosen to be the reduced wave vector (k normalized to the Brillouin zone size $k_{\Gamma X}$). To highlight the thermal effect, Fig. 3(b) shows $E(k)$ at three different reduced k values as a function of T. The points represent results derived from both 14 and 19 ML films. The temperature coefficient changes sign at a reduced k slightly larger than 0.800, i.e., very close to the Fermi level. A simple explanation for our observation is that as the lattice expands, the interatomic overlap integral decreases, and therefore the band dispersions should decrease. This is consistent with our finding that the high temperature band structure has a smaller slope. Because of charge conservation, the low and high temperature bands should coincide near the Fermi level, again in qualitative agreement with our observation. This implies a very small temperature dependence for the reduced Fermi wave vector $k_F/k_{\Gamma X}$.

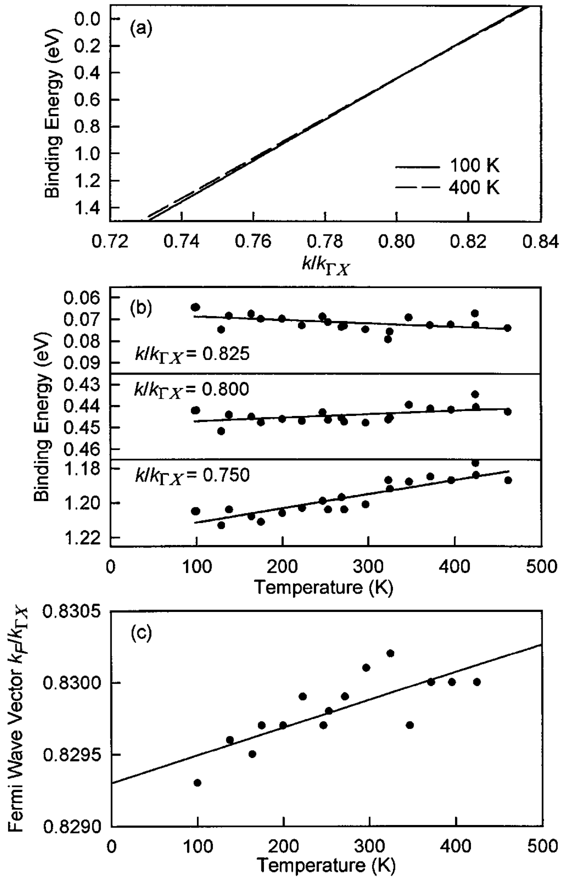

FIG. 3. (a) Ag sp-band dispersion at 100 and 400 K in the ΓX direction plotted as a function of the reduced wave vector $k/k_{\Gamma X}$. (b) The measured binding energy E at three different reduced wave vectors as a function of T. The straight line in each case represents a linear regression of the data. (c) The reduced Fermi wave vector $k_F/k_{\Gamma X}$ as a function of T. The straight line represents a linear regression of the data.

Figure 3(c) shows $k_F/k_{\Gamma X}$ as a function of temperature from our analysis. The extrapolated value at absolute zero temperature is $k_F/k_{\Gamma X} = 0.829 \pm 0.001$. The error given here is the systematic error as found from an analysis of Ag layers of various thicknesses. The temperature dependence observed here is indeed very small. Our value at 0 K is at variance from the value $k_F/k_{\Gamma X} = 0.819$ deduced from a de Haas–van Alphen measurement by Coleridge and Templeton [11]. The de Haas–van Alphen method is the standard method for Fermi surface measurements, and its development is widely regarded as a milestone in solid state physics. This method, however, gives only the circumference of the Fermi surface, and the determination of the Fermi wave vector depends on the precision of the parametrization of the Fermi surface. Steele and Goodrich [16] pointed out in their study of the radio-frequency size effect that the Fermi surface of Au as determined by the de Haas–van Alphen method is in fact not entirely accurate. Namely, the Fermi wave vector in the [100] direction is 1% too small. This is very similar to the 1% discrepancy (with the same sign) found for Ag in this study.

It is interesting to compare the present study of the temperature effects on valence electrons with previous studies of core levels [17,18]. In addition to the electron-phonon coupling, electronic excitations can be a significant contribution to the thermal broadening of core levels. The mathematical analysis and the information gained are quite different. Interested readers are referred to the original publications for details.

In summary, this paper presents a determination of the complex band structure of Ag as a function of temperature. The accuracy achieved by quantum well spectroscopy using atomically uniform films far exceeds what has been possible with traditional photoemission spectroscopy, thus enabling quantitative measurements of the effects of electron-phonon coupling in the bulk. The imaginary part of the band structure (lifetime broadening) is easily deduced from the quantum well peak width, and its temperature dependence provides a direct measure of the electron-phonon mass enhancement parameter. This parameter is of central importance to a number of physical effects and phenomena including heat capacity, electrical resistance, superconductivity, and tunneling. The band dispersion decreases at higher temperatures as expected. The measured temperature dependence over a wide range allows an extrapolation to absolute zero temperature, and the resulting Fermi wave vector is much more accurate than that obtained from the de Haas–van Alphen method. The latter is too small by 1%.

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