Brief Reports

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Empty electronic states of silver as measured by inverse photoemission

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We have performed inverse photoemission (bremsstrahlung isochromat spectroscopy) at $h\nu = 9.7$ eV on polycrystalline silver. Our spectrum can be related to the calculated density of unoccupied states up to 7 eV above the Fermi level E_F. Pronounced features in the isochromat spectrum are associated with critical points in the band structure of silver. We find X_6^- at $E_F + (2.1 \pm 0.1)$ eV and L_4^+ at $E_F + (3.77 \pm 0.09)$ eV. The results are compared with band-structure calculations as well as other experimental findings.

The noble metals Cu, Ag, and Au with their filled *d* shells and a conduction band with one (*s,p*) electron provide prototype systems for the understanding of the electronic structure. Accordingly, a vast number of both experimental and theoretical publications exists, which deal with the band structure, the resultant optical properties, and their modifications in going from the bulk to the surface. Most of our knowledge so far, however, is restricted to the occupied part of the electronic states or to experiments in which the joint density of occupied *and* unoccupied states is probed. Experimental work delivering direct information about the unoccupied states is scarce, although it would appear to be very fruitful, since discrepancies still exist. In particular, there is a controversy in Ag and Au about the position of the unoccupied band No. 7 which runs from Γ_6^- to L_4^+ and has *s* character. Relativistic calculations by Christensen[1,2] employing a muffin-tin potential derived from Dirac-Slater charge densities place it 0.5 to 4 eV lower in energy than could be inferred from angle-resolved photoemission in both silver[3] and gold.[4,5] The discrepancy increases with increasing electron energy (going, e.g., from L_4^+ to Γ_6^-).[5] On the other hand, the calculated[1,2] occupied bands are very well reproduced by angle-resolved photoelectron spectroscopy (ARPES).[3-5] Jepsen, Glötzel, and Mackintosh[6] in a self-consistent local-density calculation including relativistic shifts but no spin-orbit coupling obtain an L_4^+ value in agreement with experiment,[3-5] but differ with respect to the occupied bands by 0.4 to 1.4 eV.

Here, we employ the new technique[7-10] of ultraviolet inverse photoemission (bremsstrahlung isochromat spectroscopy) at $h\nu = 9.7$ eV to silver. We can determine the energies of the critical points L_4^+ and X_6^- of unoccupied bands between the vacuum level and the Fermi energy E_F. Impinging electrons with a kinetic energy $E_k > E_F$ enter the sample and get trapped in some empty states above E_F. Whereas most electrons undergo inelastic collisions during thermalization, a small fraction will lose its energy by radiative processes. For a fixed photon energy (i.e., the isochromat) the number of emitted photons is a direct mea-

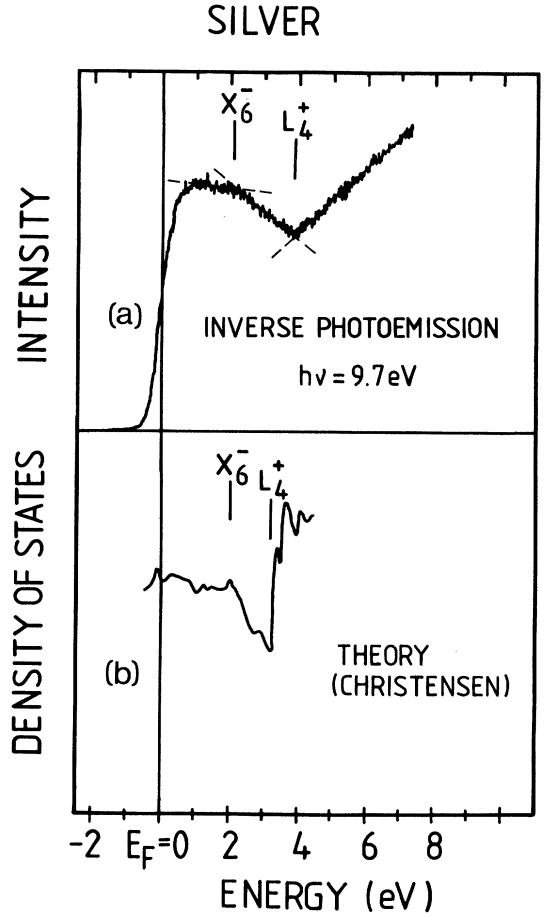

FIG. 1. (a) Isochromat spectrum at $h\nu = 9.7$ eV from polycrystalline silver. The broken lines indicate linear fits to parts of the spectrum to obtain the kink at 2 eV and the minimum around 3.8 eV. (b) Calculated total density of states from Ref. 1 [normalized to the spectrum in (a) at 2 eV]. The positions of the critical points are given. The agreement for X_6^- with the experimental value in (a) and the disagreement for L_4^+ are discussed in the text.

sure of the available density of empty states at a given E_k.[11] The onset of photon emission as a function of E_k is then referenced to the Fermi level (usually the energy zero, $E_F \equiv 0$).

The experiment is performed in an ultrahigh-vacuum (UHV) chamber (base pressure 3×10^{-10} Torr) equipped with a 180° concentric hemispherical analyzer[12] for Auger-electron spectroscopy (AES). Electrons from a custom-made electron gun with a BaO cathode[13] hit a sputter-cleaned polycrystalline silver foil. Outcoming photons of $h\nu = 9.7$ eV are filtered and detected by an UHV-compatible Geiger-Müller counter[14] using the concept proposed by Dose and co-workers.[7] With primary beam currents around 15 μA, the count rates are typically 600 cps with a dark rate of 5 per minute. With use of a multichannel analyzer, a typical (as in Fig. 1) isochromat spectrum of 512 channels averaged over 32 sweeps ($5.0 \leq E_k < 15$ eV) takes 15 min. The overall resolution (electrons and photons) can be inferred from the onset of photon emission (corresponding to E_F). For the 90%–10% intensity rise in Fig. 1(a) we find $\Delta E = 0.7$ eV. Any contamination (mostly O) of the silver foil stayed below the AES detection limit before and after the inverse-photoemission measurement.

In Fig. 1(a), we present an isochromat spectrum at $h\nu = 9.7$ eV for polycrystalline silver. The onset of emission at E_F is followed by a plateau. After a kink around 2 eV, the intensity decreases linearly to a minimum around 3.8 eV, followed by an increase in intensity at higher energies. The latter increase is typical for isochromat spectra[7–10] and reflects background emission due to electrons which have suffered inelastic processes before emitting a 9.7-eV photon. The intensity minimum is very sensitive to contamination. In a separate study,[15] we found that this minimum was filled up and the intensity near E_F was already lowered at an O_2 adsorption level which could hardly be detected by AES.

The polycrystalline nature of the silver sample ensures that we measure the total density of states (DOS) and not a $\vec{k}$-projected DOS as in cases of angle-resolved inverse photoemission on single-crystal surfaces.[9,10] Therefore, in Fig. 1(b), we compare the spectrum of Fig. 1(a) with the calculated total DOS of Ref. 1. The qualitatively similar DOS calculated nonrelativistically by Rijsenbrij and Fondse,[16] although extending into the same energy range, agrees even less with our spectrum, therefore, we prefer Christensen's DOS. The two critical points X_6^- and L_4^+, which produce pronounced features in the theoretical DOS, can be associated with our kink at 2 eV and the minimum around 3.8 eV. Using linear fits to parts of the spectrum [indicated in Fig. 1(a) by broken lines], we find X_6^- at $E_F + (2.1 \pm 0.1)$ eV and L_4^+ at $E_F + (3.77 \pm 0.09)$ eV.[17] These numbers are the mean values from eight independent measurements. The errors give the standard deviations, respectively.

In Table I, we compare our results for X_6^- and L_4^+ with the calculated values of Christensen,[1] Jepsen *et al.*,[6] and Rijsenbrij and Fondse.[16] We have also included values calculated by Fong, Walter, and Cohen[18] and Chen and Segall,[19] who used empirical, nonlocal model potentials, and of Lässer, Smith, and Benbow,[20] who applied a combined interpolation scheme to fit Christensen's bands. Finally, the experimentally[21,22] obtained energy position of the L_4^+ point is shown in Table I. The X_6^- point has so far not been measured at all. It can now serve as a new test in addition to the L_4^+ point.[23]

We note that our L_4^+ value agrees well with the other numbers derived experimentally in the last column of Table I, which gives us confidence in the new technique of inverse

TABLE I. Comparison of several theoretical and experimental critical-point energies in silver (no claim to being complete).

Work by	Method	Potential	Relativistic	First principles	Self-consistent	Energy above E_F (eV) X_6^- (X_4')	Energy above E_F (eV) L_4^+ (L_1)
Christensen (Ref. 1)	Augmented plane wave	Atomic potential with muffin tin, $\alpha = 1$	Full	Yes	No	2.02	3.33
Jepsen *et al.* (Ref. 6)	Augmented plane wave	Local density with atomic-sphere approximation	Yes, no spin orbit	Yes	Yes	1.70	3.79
Rijsenbrij and Fondse (Ref. 16)	Korringa-Kohn-Rostoker	Atomic potential with muffin tin $\alpha = 1$	Semi	Yes	No	1.75	3.3
Fong *et al.* (Ref. 18)	Empirical nonlocal pseudopotential	Fit to optical and photoemission data	No spin orbit	No	· · ·	1.75	3.7
Chen and Segall (Ref. 19)	Empirical Korringa-Kohn-Rostoker	Fit to Fermi surface and optical gaps	No spin orbit	No	· · ·	1.84	3.88
Lässer *et al.* (Ref. 20)	Combined interpolation	Fit to Christensen's bands (Ref. 1)	With spin orbit	No	· · ·	1.75	3.6
Nilsson and Sandell (Ref. 21)	Reflectance					· · ·	3.8
Rosei, Culp, and Weaver (Ref. 22)	Thermoreflection and thermo-transmission					· · ·	3.85
Present authors	Inverse photoemission					2.1 ± 0.1	3.77 ± 0.09

photoemission. In addition, the empirical methods (Refs. 18 and 19) have used experimental values for the gap at the L point ($L_4^- \rightarrow L_4^+$) as input parameter; therefore, agreement with our data is not surprising. On the contrary, their values for the X_6^- point are too small by ~ 0.2 eV, indicating how much these methods have to rely on the proper choice of input parameters. Amongst first-principles calculations (Refs. 1, 6, and 16), the nonrelativistic one of Ref. 16 using a relativistic potential gets both critical-point energies off by 0.35 and 0.5 eV, which shows that relativistic effects in Ag are to be taken into account. This leaves us with the two best calculations available today, i.e., Refs. 1 and 6. Interesting enough, both calculations agree and disagree with our experiment with respect to one critical point. Christensen's calculation provides the best agreement for the X_6^- point (as well as for the occupied bands probed[3] by ARPES). Jepsen *et al.*,[6] however, agree on the L_4^+ point, but as with the unoccupied bands[6] their X_6^- point energy is too low by 0.4 eV. The suggestion of Jepsen *et al.* to include self-energy corrections to the excitation energies to improve agreement with ARPES does not seem to be the solution. Indeed, relaxation energies are expected to be smaller in inverse photoemission than in photoelectron spectroscopy, while the disagreement with theory[6] is equally large. Rather, we believe that relativistic effects influence the position of the L_4^+ point (mostly s-like) more than the X_6^- point (some p character), resulting in too big a downward shift of L_4^+ in Ref. 1. New fully relativistic *and* self-consistent calculations would help to clarify this problem.

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