Valence-Band Dispersion in Angle-Resolved Resonant Photoemission from LaSb

C. G. Olson
Iowa State University

P. J. Benning
Iowa State University

Michael Schmidt
Iowa State University, mike@si.fi.ameslab.gov

David W. Lynch
Iowa State University, dlynch@iastate.edu

Paul C. Canfield
Iowa State University, canfield@ameslab.gov

See next page for additional authors

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Abstract
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Keywords
Ames Laboratory, Bloch component, RESPES, Costers-Kronig

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Authors
C. G. Olson, P. J. Benning, Michael Schmidt, David W. Lynch, Paul C. Canfield, and David Michael Wieliczka
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C. G. Olson, P. J. Benning, Michael Schmidt,* D. W. Lynch, and P. Canfield

Department of Physics and Astronomy and Ames Laboratory, U.S. DOE, Iowa State University, Ames, Iowa 50011

D. M. Wieliczka

Department of Physics, University of Missouri–Kansas City, Kansas City, Missouri 64110
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Angle-resolved photoemission spectra taken on single crystals of LaSb at the La $4d \rightarrow 4f$ resonance show dispersion of resonantly emitted valence-band electrons. This is the first direct demonstration that the Bloch component of valence states participates in resonant photoemission. [S0031-9007(96)00307-9]

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Resonant photoemission (RESPES) is a widely used technique for studying the electronic structure of atoms and solids [1–6]. Hereafter it has been treated as an atomic or localized phenomenon, as described below. Any observed angle dependence appeared in the magnitude of the photocurrent, not in the energy of the photoelectrons [7]. A possible exception to this is the 30 meV dispersion seen near the Fermi level $E_F$ in CePt$_2$Al$_3$ by Andrews et al. [8]. In the following we report the dispersion of resonantly emitted valence-band electrons in LaSb, which suggests that the wave vector remains a good quantum number for this process despite the Coulomb matrix element in Auger decay. No momentum-independent emission that could be attributed to a resonant Auger process is seen.

In RESPES a core electron is excited to a state in an incomplete subshell that is well localized on the site of the core hole so the dipole matrix element for the excitation process is large [9]. One decay channel for the excited state is an Auger process [10], refilling the core hole and ejecting as a photoelectron an electron from one of the localized states or from the valence band. When the Auger process is a super Costers-Kronig (SCK) process, the transition rate is unusually large. These processes can give a large resonance in the photoelectron spectrum as a function of photon energy. More correctly, the series of events just described cannot be treated as individual, time-ordered energy-conserving events. Quantum mechanics requires treating the transition between the initial and final states as a single process. Since direct photoemission from the initial state can lead to the same final state as one of the aforementioned decay processes, the shape of the resonant photoemission spectrum may be altered by interference between these processes. The photoexcitation cross section for direct photoemission is usually slowly varying with photon energy at the core-level resonance energy. The two amplitudes must be added before squaring in the total cross section, leading to interference phenomena and “Fano” line shapes [11]. Examples are photoelectrons from the $3p \rightarrow 3d$ transitions of $3d$ transition metals and the $4d \rightarrow 4f$ transitions in lanthanides [1]. Both can give rise to SCK processes. All previous studies of RESPES, both theoretical and experimental have been interpreted with a localized picture; all states were described with quantum numbers appropriate for systems with spherical symmetry or as crystal-field-split localized levels. The latter, even when hybridized with ligand orbitals, may show anisotropy in the emission intensity, but not dispersion in energy as the emission angle is varied. Angle-resolved RESPES in LaSb, however, shows dispersion with the wave vector, as shown below.

The measurements were carried out on single crystals of LaSb, a rock-salt structured semimetal. The valence bands are composed primarily of Sb $5p$ states which hybridize with La $5d$ states [12–15]. The $4f$ levels lie about 2 eV above $E_F$, but they hybridize significantly with the valence band. A full description of angle-resolved photoemission from LaSb, CeSb, NdSb, PrSb, and YSb will be published elsewhere [16]. The crystals were cleaved in situ at 20 K in a vacuum of a few times $10^{-11}$ Torr, exposing a (100) face, stable for several days in vacuum. Angle-resolved photoemission spectra were collected using a hemispherical analyzer. Photons from an ERG monochromator on the Ames-Montana State beam line on Aladdin [17] were incident at an angle of 40° for all measurements reported here. The energy resolution was 250 meV and the angle resolution 2° full angle.

Figure 1 shows representative angle-integrated energy distribution curves (EDCs). LaSb has an overall valence bandwidth of about 3.7 eV, with a very low density of states at $E_F$. The 118 eV EDC is at the $4d \rightarrow 4f$ adsorption maximum, but with no occupied $4f$ states in the formal valence there is not the large enhancement of the photoemission strength that would be seen in compounds of Ce or heavier rare earths. Figure 2 contains the total yield spectrum, essentially the absorption spectrum, through the $4d$ resonance absorption. The sharp yield peak at 101.5 eV is from the $4d \rightarrow 4f \ ^3D_1$ excited state. The large, broad structure at higher energy is from the autoionizing $^1P_1$ excited state. These multiplets result from
the strong exchange and Coulomb interactions between the 4d hole and the single 4f electron in the final state in absorption. These interactions are very large due to the similar radii of the 4d and 4f wave functions.

Angle-resolved constant initial state (CIS) spectra taken in normal emission are also shown in Fig. 2 for initial states at various binding energies in the valence band, those marked in Fig. 1. Conventionally, resonance effects are determined by comparing spectra taken on (118 eV) and off (110 eV) resonance, as determined from the yield or absorption spectrum. However, as can be seen in Fig. 1, even the angle-integrated EDCs still change shape with photon energy. Instead, to isolate resonance effects from nonresonant changes in the valence band emission, spectra on the fine-structure resonance at 101.5 eV have been compared with off-resonance spectra taken at 101 or 102 eV. This means that there are negligible changes in the photon-energy dependent, nonresonant cross sections or matrix elements. Changes in wave vector \( k \) due to electron kinetic energy are small compared to the \( k \) resolution limitation from the 2° angle acceptance. The broad peak at 105 eV in the top CIS is a consequence of the CISs being angle resolved and will be discussed in the context of Fig. 3.

There is support in the CIS spectra for the identification of hybridization in the Sb 5p valence band with La 5d and 4f states. The changes in the derivativelike shape of the 101.5 eV feature in the CISs of Fig. 2 indicate a change in valence band character with binding energy. The latter is evident also in the shift of weight between the two features at 116–118 eV in the main resonance. Similar spectra in the main resonance for two phases of Eu [18] make a strong case for the assignment of the resonance at lower photon energy to the 5d, and the one at higher energy to the 4f. This is supported by a theoretical study by Zangwill and co-workers [3,6], who calculated the cross sections for the emission of photoelectrons from various subshells, e.g., 4f, 5d, 6s, after photoexcitation of a 4d electron of the Ce atom. Subsequently these cross sections were measured in Ce and La vapor by Meyer and co-workers [19,20] with good, but not perfect, agreement. Zangwill found that as one scanned through the 4d photoexcitation from low photon energy to high, the subshell emission resonances peaked at increasing energies as the average radius of the subshell electrons decreased. The photoemitted electrons need not have 4f character to exhibit resonant effects.

Figure 3 shows angle-resolved EDCs taken over a range of angles such that the range of the wave vector component parallel to the surface spans the Brillouin zone. In each pair the upper curve is on resonance, the lower, off resonance. The spectra are normalized to the incident photon flux. As can be seen from the lower, nonresonance, curve at each angle, valence-band dispersion still dominates the spectra at these photon energies.
energies. Since equivalent changes in the perpendicular component of \( \mathbf{k} \) would have a similar effect, it is important that the angle-dependent (parallel component of \( \mathbf{k} \)) changes be determined with small changes in photon energy. Similar spectra comparing EDCs taken at 118 and 110 eV also show large angle dependencies, but the difference structures are not as well defined and do not have as simple a relationship to the crystal. The broad peak at \( h\nu = 105 \) eV in the 2.5 eV binding energy CIS is another example of the effect of momentum resolution.

Even though the CISs were taken in normal emission, the changing photon energy means that the momentum acceptance window moves along a line between \( X \) and \( \Gamma \). Changing densities of states give rise to broad features such as the 105 eV peak.

The difference between the upper and lower EDCs of Fig. 3 are shown in Fig. 4. The changes in the difference curves with angle result only from changes in the resonant enhancement of the valence band emission across the Brillouin zone. The peak shifts with angle are manifest. The absence of a background component indicates there is no resonant enhancement of an Auger process.

Extensive angle-resolved measurements on CeSb [16] have allowed an accurate determination of the inner potential, hence the placement of bands in the three-dimensional Brillouin zone. The LaSb spectra can be compared with those of CeSb at low energy where the 4\( f \) cross section is small to determine the perpendicular component of \( \mathbf{k} \). At the resonant photon energy and normal emission, the region near \( X \) is being sampled. As the angle is increased in Figs. 3 and 4, the states sampled are not along high symmetry lines, but follow an arc from \( X \) (100) through \( W \) (101/2), towards \( \Gamma \). According to recent self-consistent local density approximation (LDA) calculations [15] the occupied states near \( E_F \) at \( X \) have a large La 5\( d \) contribution. This state disperses through \( E_F \) away from \( X \). The changes in the first 1 eV in Fig. 4 are consistent with this behavior.

The lowest conduction band in LaSb has its minimum at the \( L \) points in the Brillouin zone, 3.0 [15] or 3.6 eV [12] below \( E_F \), according to recent self-consistent LDA calculations. This corresponds to the 3.7 eV bandwidth seen in the angle-integrated EDCs of Fig. 1. The calculations also predict the ca. 30% narrower bandwidth in the \( X-W-\Gamma \) regions sampled in the geometries of Fig. 3. The largest fraction of La 5\( d \) character is near \( E_F \) at \( X \), with some hybridization throughout the valence band. This can be verified by comparing the on- and off-resonance curves of Fig. 3. The CIS spectra support the assignment of a very small amount of 4\( f \) character to the slowly dispersing feature at 2.5 eV in the difference curves. LaSb is a very fortunate case in that the perpendicular momentum resulting from the resonant photon energy corresponds to a crystal momentum with a large admixture of 4\( f \) character.

Davis and Feldkamp [4] have applied the model of Fano to photoemission, and Davis [5] gave numerical computations for 3\( d \) transition metal oxides and halides, both for angle-integrated photoemission. The Coulomb
matrix element is at the heart of the theory, for it is responsible for the nonradiative decay of the excited state. Wave vector conservation is unexpected. However, as pointed out by Wendin [21], the many-body effects resulting from the Coulomb (and exchange) interaction need not be considered in the initial- and final-state wave functions in the matrix elements. They can be incorporated in the operator, as Zangwill has done. Thus the bare Coulomb potential with many-electron states in the Auger matrix element mentioned above need not be used. However, the use of Bloch functions with Zangwill’s time-dependent RPA-local field approach has not yet been carried out.

Dispersion in RESPES may be a widespread phenomenon, but not previously observed because of strong overlapping contributions from 4f electrons that do not disperse. It is important to put the magnitude of the effect in perspective to understand why this effect is seen so clearly in LaSb and not, e.g., in CeSb. With its occupied 4f states, the CeSb valence band emission above resonance is 30 times stronger than that of LaSb. The atomic-like 4f resonant emission dominates in compounds of Ce and heavier lanthanides. Higher-lying valence states in LaSb and all valence states in CeSb may show such dispersion, but it will be obscured by a large contribution from the 4f admixture which disperses far less, if at all.

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*Current address: Forschungszentrum Karlsruhe, INFP, Karlsruhe, Germany.