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Ultraviolet photoelectron spectroscopy of PbTe: Direct versus nondirect transitions and energy-loss mechanisms

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In the present paper the interpretation of recent experimental results on ultraviolet photoelectron spectroscopy of PbTe is given. It is pointed out that the photon energy dependence of the position of the main structures in the energy distribution curves (EDCs) cannot be explained either in the direct or in the nondirect model, if one calculates the primary EDCs, i.e., if transport and escape effects are neglected. The energy loss suffered by photoelectrons owing to phonon scattering is introduced in a simple and realistic model in which one accounts for the $\vec{k}$ dependence of the velocity of hot photoelectrons and for the velocity dependence of electron-phonon scattering cross section. In the three-step model of photoemission this $\vec{k}$ and velocity dependence couples the first and the second step; this fact is relavant in the interpretation of experimental results. The present calculations based on the proposed model rely upon the relativistic empirical-pseudopotential-method band calculations and give a satisfactory agreement with experimental results within a direct transition scheme. A nondirect transition scheme is not satisfactory even if transport effects are included. The validity limits of the model are discussed and it is shown that its relevance is beyond the case of PbTe spectroscopy which is treated here.

I. INTRODUCTION

The ultraviolet photoelectron spectroscopy (UPS) of PbTe has been the subject of experimental investigation by Spicer and Lapeyre[1] and by Abbati *et al.*[2] with photon energy below LiF cutoff, and by Cardona *et al.*[3] at $\hbar\omega = 21.2$ eV. The energy distribution curves (EDCs) of PbTe given in Refs. 1 and 2 have been regarded as experimental evidence of direct transitions. In particular this fact was considered evidence for the behavior at various photon energies of two prominent structures seen on the high-energy side of the EDCs; these are labelled P_3 and P_4 in Ref. 2 and are clearly seen in Fig. 1(a), where the EDC at $\hbar\omega = 7.75$ eV measured by Abbati *et al.*[2,4] is given. These structures were assigned to a pair of nearly flat bands along the Λ line near L where they are spin-orbit split with symmetries L_6^+ and L_{45}^+ (second and third valence bands from the top). A typical feature of structures P_3 and P_4 is the fact that the energy interval δ between them is not constant when the photon energy is changed. In the interval $7 < \hbar\omega < 9$ eV the results in Ref. 2 give the values plotted in Fig. 1(b) (line 1); around $\hbar\omega = 9.5$–11 eV, Spicer and Lapeyre[1] found that the structures disappear, while they were resolved at $\hbar\omega = 21.2$ eV by Cardona *et al.*,[3] who measured $\delta = 0.45$ eV. McFeely *et al.*[5] could not resolve the structures with x-ray photoelectron spectroscopy (XPS) but found analogous structures in PbS and PbSe.

On the other hand, recent theoretical works have cast heavy doubts upon the possibility of interpreting these experimental results on the basis of a direct model. Valence-band density of states were calculated by Buss and Schirf[6] with the augmented-plane-wave–liner-combination-of-atomic-orbital method, by Kohn *et al.*[7] and by Ciucci *et al.*[8,9] with the empirical pseudopotential method (EPM); all these densities of states show two sharp structures which correlate well with (P_3, P_4) [Fig. 1(a)], and it is extremely unlikely[10] that final-state effects, in the theoretical EDCs, modify drastically at different $\hbar\omega$ the position of the structures (P_3, P_4). This fact is confirmed by the theoretical results which are summarized in line 2 of Fig. 1(b), where the values for the primary EDCs (i.e., without transport and escape effects) calculated in the direct scheme are reported; these values are obtained from the EDCs computed from the EPM bands of PbTe by Ciucci and Nardelli.[9] On the other hand, a computation of the EDCs in the nondirect model based on the same bands gives a nearly constant δ value (0.6 eV). Moreover (P_3, P_4) in the theoretical EDCs cannot be assigned as in Refs. 1 and 2 but must be attributed to the first and second (from the top) valence bands. This is confirmed by the analysis of the band density of states.[8,9] All these results show that neither a direct nor a nondirect model can explain the experimental results. [A further computer work carried out by the present authors showed that also an intermediate model (partial $\vec{k}$ conservation represented with a suitable broadening) fails in the present case.] The disagreement between theory and experiment can hardly be due to inadequacies of the bands since all the bands quoted

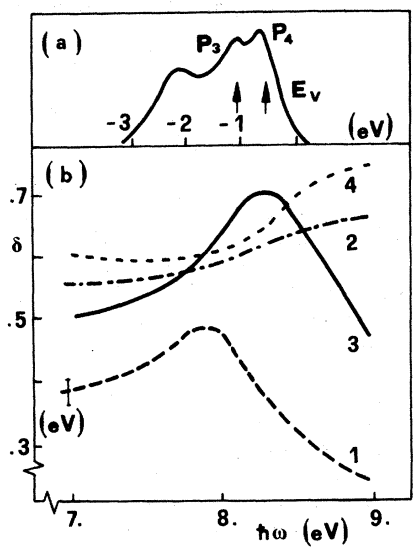

FIG. 1. (a) PbTe EDC at $\hbar\omega = 7.75$ eV (Ref. 4); E_v is the extrapolated upper valence edge. The arrows indicate the corresponding peaks in the density of states by Ciucci and Nardelli (Ref. 9). (b) δ: curve 1, experimental from Ref. 2, the error bar indicates the upper limit of the experimental uncertainty which is constant in the whole plot; curve 2, direct-model calculation without energy loss; curve 3, direct model with energy loss to phonons; curve 4, nondirect model with energy loss to phonons.

above give excellent optical constants; furthermore the calculations of EDCs are very reliable as explained below. On the other hand, the measured variation of δ with $\hbar\omega$ is far beyond the uncertainties of the experiment (see below).

The purpose of the present paper is to give a way out from this situation by considering in the calculation the effect of the electron-phonon scattering suffered by hot photoelectrons before emission. The paper shows, also, that the relevance of the treatment presented here lies beyond the case of PbTe which stimulated the present research.

II. EXPERIMENTAL AND THEORETICAL RESULTS USED IN THE PRESENT PAPER

The experimental basis of the paper is the set of measurements from which is derived Ref. 2. Line 1 of Fig. 1(b) is taken from this reference and a new accurate analysis of the experimental results has been done in order to establish the limits of uncertainty in the curve; these limits resulted in values lower than 20 meV. In this connection it is possible to state what follows: (i) The phenomenology excludes that background effects can cause an artifact in the variation of δ with $\hbar\omega$: the results taken from the EDCs and those from their first derivative (measurement of the second harmonic with retarding field apparatus) are coincident within 10 meV. Furthermore, a computer analysis based on the assumption of two structures and of reasonable background of scattered electrons excludes the possibility of background effects in line 1 of Fig. 1(b). (ii) The results taken with different modulation amplitudes (120, 200, 250 meV peak to peak) are coincident within noise. In this connection a computer analysis based on the theory of instrument response function[11-13] excludes this possibility of artifacts; furthermore the influence of the higher derivatives contained in the measured harmonic has been recognized to be very small (lower than 10 meV).

The theoretical work summarized below is based on the band calculations by Ciucci and Nardelli.[9] This is a relativistic EPM calculation of bands and dipole matrix elements in 182 points of the irreducible segment of the Brillouin zone (BZ). The present treatment requires a detailed knowledge of the bands and this is achieved with a least-square quadratic interpolation scheme in about two million points randomly distributed in the irreducible segment of the BZ. As already said these bands are satisfactory; there might only be a slight uncertainty in the absolute position in the energy scale of the higher conduction bands (from 9th to 18th band of Ref. 9) due to the truncation of the pseudo-Hamiltonian matrix. For this reason attention has been concentrated upon the photon energy range up to 9 eV considering the results of Ref. 2 which refer to the (100) face of cleaved PbTe. No attempt is done to interpret, in detail, the pioneering results by Spicer and Lapeyre[1] taken over evaporated films whose morphology is not characterized; nevertheless it is worthwhile to note the general agreement between the experimental results of Refs. 1 and 2.

III. DISCUSSION OF THE MODEL

Since the calculation of the primary EDCs cannot explain experimental results it is necessary to consider the transport effects as are shown here. The energy loss processes, which might be responsible for the dependence of δ on $\hbar\omega$, were considered. The energy loss due to electron-electron scattering cannot generate this behavior since an e-e collision removes electrons from the structures. It is necessary to rely upon energy losses which are small with respect to the kinetic energy of the photoelectrons, and the effect of electron-phonon collisions has been considered. This process has been treated within a model which constitutes a reasonable simplification of the problem, while it gives a realistic description of the process. The main hypotheses of the model, which is even sim-

pler than that by Kane[14] are summarized here.

(i) An energy loss

$$\Delta E = \sqrt{3}\, L \langle E_p \rangle / l_p \tag{1}$$

is introduced, where L is the escape depth, the factor $\sqrt{3}$ coming by the three-dimensionality of the problem[14] and $\langle E_p \rangle = \langle E_{\rm ph}/2n+1 \rangle$ is the phonon energy averaged over phonon occupation numbers; this expression obviously takes into account absorption and emission of phonons; l_p, the electron phonon (e-p) mean free path, is assumed to be dependent on the electron group velocity v_g through $l_p = v_g/f$, where f is a constant collision frequency and $v_g = |\vec{\nabla} E_c(\vec{k})/\hbar\omega|$ (E_c is the electron energy in the conduction band). A similar velocity dependence of the e-p cross section has been assumed by Kane[15] in Ge. In the photon energy range considered here an average value $L = 35$ Å is assumed in PbTe from the measurements by Pong.[16]

(ii) For electron energies like those in the present case (about 5–9 eV above the top of the valence bands) the e-p coupling is both with acoustical modes near the boundary of the BZ and with the optical modes (the Debye temperature[17] of PbTe is 130 K) as pointed out in Refs. 18 and 19, where it is shown that in both cases the scattering cross section is peaked in the forward direction; for these reasons, in PbTe we have used the value of the longitudinal optical phonon.[20]

(iii) For each conduction band the following calculation has been made: for each energy E' of the primary EDC a corresponding contribution to the EDC after slowing down is obtained at the energy $E' - \Delta E$, where ΔE is calculated as in (i) by means of a group velocity which is the average of the values pertaining to all the final states contributing to the primary EDC at this energy; i.e. the following relations have been employed:

$$N'(E, \hbar\omega) = \sum_c \int\int N_c(E', \hbar\omega)\, \delta(E - E' + \Delta E_c)\, dE'\, d\Delta E_c , \tag{2}$$

where N' is the EDC after slowing down, N_c is the contribution (computed in the direct or nondirect case) to the primary EDC due to transitions up to the conduction band c. The energy loss ΔE_c is given by (see Ref. 1): for the direct transition model

$$\Delta E_c(E', \hbar\omega) = \sqrt{3}\, L E_p f \frac{\sum_v \int d^3k\, \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)\, \delta(E' - E_c(\vec{k}))}{\sum_v \int d^3k\, v_g(\vec{k})\, \delta(E_c(\vec{k}) - E_v(\vec{k}) - \hbar\omega)\, \delta(E' - E_c(\vec{k}))} , \tag{3}$$

and for the nondirect transition model

$$\Delta E_c(E', \hbar\omega) = \sqrt{3}\, L E_p f \frac{\sum_v \int\int d^3k\, d^3k'\, \delta(E_c(\vec{k}) - E_v(\vec{k}') - \hbar\omega)}{\sum_v \int\int d^3k\, d^3k'\, v_g(\vec{k})\, \delta(E_c(\vec{k}) - E_v(\vec{k}') - \hbar\omega)} . \tag{4}$$

v_g is the module of the group velocity and E_v is the energy in the valence bands.

Thus the energy loss straggling is neglected and the average energy loss is calculated with reference to the velocities before slowing down. This approximation greatly simplifies the calculations and is legitimate if the set of $\vec{k}$-space points reached during slowing down is not very different from the set representing the states before slowing down; this is the case when the e-p cross section is forward peaked [see (ii)]. Within the above model the δ values for the EDCs after slowing down were evaluated as a function of $\hbar\omega$ by choosing the best value of f. Since the structures P_3 and P_4 appear 2–3 eV above the vacuum level the description of escape is not critical; an escape probability equal to 1 was assumed when (after slowing down) the energy associated with a momentum normal to the (100) face is over the vacuum level.

IV. RESULTS AND DISCUSSION

If one assumes a direct scheme and the effect of e-p collision is taken into account within the model given above, one obtains the best results with $f = 6.22 \times 10^{14}$ sec^{-1}; the EDCs after slowing down are calculated with a Lorentzian broadening consistent with the used f value. The resulting values are given in line 3 of Fig. 1(b) as a function of $\hbar\omega$. In the nondirect scheme the results are given by line 4 of Fig. 1(b); the f value is the same as in the direct case since no improvement was possible by adjusting f.

The agreement of the results in the direct scheme with the experiment of Ref. 2 is very satisfactory

and nearly quantitative; no special meaning must be attributed to the 30% disagreement in δ and 6% disagreement in $\hbar\omega$, which are probably due to the possible inaccuracy in the position of the higher conduction bands (see Sec. II).

These results show the success of the present treatment in which the electron-phonon energy loss is included in the calculation of the EDCs. In this connection one can state what follows:

(i) The structures P_3 and P_4 of the EDCs and PbTe must be attributed to direct transitions but for reasons different from those assumed in Refs. 1 and 2. The energy loss is sensitive, through the velocity dependence of the e-p cross section, to the nature of the states of hot photoelectrons: in the direct scheme the set of final states changes considerably with $\hbar\omega$ and this explains the $\hbar\omega$ dependence of δ, while in the nondirect case the energy loss is averaged over too large a $\vec{k}$-space region (the whole set of points having energy corresponding to that of the considered structures) so that this dependence is obliterated.

(ii) The present method gives an indirect measurement of the e-p collision frequency at electron energies at which it would be hard to obtain it with other methods. The value $f = 6.22 \times 10^{14}$ sec^{-1} is consistent with an estimate based on Seitz's[17] treatment.

(iii) Typical e_p values obtained from the present calculations are slightly lower than 10 Å, so that from Kane's relation[14] between L, l_p, and l_e one obtains l_e of the order of 200 Å; these values testify the internal consistency of the treatment in which $l_p \ll l_e$ is assumed. The present mean free paths differ from those obtained by Pong[16] but agree with the low intensity of the secondary electron peak in the EDCs measured in the 10^{-11}-Torr range.[2]

(iv) The model is based on hypotheses which are not restrictive[17,18] and can be applied to a great variety of cases. The present results show the usefulness of considering e-p scattering in order to interpret accurately the EDCs, while until now (to the author's knowledge) e-p scattering has been considered only when it gives dramatic effects as in cesiated GaAs.[21]

V. CONCLUSION

In the present work it is clarified how a direct model with energy loss to phonons can explain recent accurate results of UPS on PbTe. It is worthwhile noting that the interest of this treatment is beyond the particular case of PbTe considered here, because the results show the importance of considering, within the three-step model of photoemission, the coupling of the three steps through the velocity dependence of the e-p cross section; this belief is analogous to that of Ref. 22, where the velocity dependence of e-e collisions is considered successfully. Furthermore the present model is more general than could appear from application to PbTe spectroscopy; when the condition $l_p \ll l_e$ is not satisfied it can still be used provided that the number of scatterings is calculated from Kane's treatment.[14]

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