Spectroscopic evidence for temperature-dependent convergence of light- and heavy-hole valence bands of PbQ (Q = Te, Se, S)

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Abstract – We have conducted a temperature-dependent angle-resolved photoemission spectroscopy (ARPES) study of the electronic structures of PbTe, PbSe and PbS. Our ARPES data provide direct evidence for the light-hole upper valence bands (UVBs) and hitherto undetected heavy-hole lower valence bands (LVBs) in these materials. An unusual temperature-dependent relative movement between these bands leads to a monotonic decrease in the energy separation between their maxima with increasing temperature, which is known as band convergence and has long been believed to be the driving factor behind extraordinary thermoelectric performances of these compounds at elevated temperatures.

Introduction. – Lead chalcogenides PbQ (Q = Te, Se, S) are canonical systems for fundamental studies of thermoelectric (TE) properties [1–3] due to their unique electronic structures. Recently, new concepts of “all scale hierarchical architecture processing” [4–6] have led to significant advancements in their TE performance. For instance, p-type nanostructured PbTe holds the current performance record for high-temperature energy conversion [7–9]. Despite being studied for decades PbQ consistently surprise us with new findings. One such example is the recently discovered appearance of local Pb off-centering dipoles on warming without a structural transition in PbTe [10,11]. Moreover, these systems have recently been shown to host various novel quantum states of matter. For instance, Pb$_{1-x}$Sn$_x$Se, Pb$_{1-x}$Sn$_x$Te are shown to be topological crystalline insulators [12–20], while superconductivity along with normal state charge Kondo anomaly occurs in Tl-doped PbTe [21].

In a number of reports, T-dependent thermopower of PbQ has been interpreted in terms of a relative shift with increase in T [8,9,22–25] between two different valence bands —namely, the upper valence bands (UVBs) with maxima at L points and the lower valence bands (LVBs) due to secondary valence bands presumably occurring along Γ-K and Γ-X lines with maxima at lower energies compared to the UVBs [22,26,27]. Despite the similarity in the findings of these studies, there is a marked disagreement among the reported values of the crossover temperatures, i.e., T’s at which separations between maxima of UVBs and LVBs vanish. For example, early works going back to the 1960s and also some of the later ones obtained a crossover T $\sim$ 450 K in PbTe, while it has recently been shown to be much higher $\sim$ 750 K [23,24]. More importantly, there is no direct experimental evidence for T-dependent changes in valence bands. Furthermore, there are recent alternative descriptions to the two-band analysis of thermopower data [28,29]. Given all these, an in-depth examination of the electronic structures of these compounds as a function of T using ARPES is highly desirable.

Recently, there have been a number of important ARPES works [13–15,30,31], on PbTe and PbSe, which are predominantly focussed on topological aspects of their electronic structures. In this article, employing T-dependent ARPES measurements on PbQ, we resolve a lingering issue in the field: How does rising T impact their valence bands? Here, we show that: i) there are two distinct valence band maxima, separated in energy as well
and 0 were collected at 2 or 4 meV energy intervals. The energy samples. ARPES measurements were performed using R4000 electron analyzer. In this work, we present ARPES crystal samples at the PGM beamline of Synchrotron (b) two analogous plots for n-type PbSe at $\bar{\sigma} = -500$ meV and $-900$ meV, respectively, while (d), (g) are for n-type PbS at $\bar{\sigma} = -500$ meV and $-950$ meV, respectively. Blue lines in (e), (f) and (g) denote cut 1 along which ARPES data have been taken for figs. 2(b), (f) and (j), while red lines correspond to cut 2 along which ARPES data have been taken for figs. 2(d), (h) and (l). Blue and red dots correspond to the momentum locations of the top of the UVBs and LVBs, respectively.

as in momentum, and ii) the energy separation between these maxima decreases with increasing T up until our highest measured T’s.

**Experiments.** – We have carried out T-dependent ARPES experiments on various n- and p-type PbQ single-crystal samples at the PGM beamline of Synchrotron Radiation Center, Stoughton, Wisconsin using a Scienta R4000 electron analyzer. In this work, we present ARPES data from a) one n- and two p-type PbTe samples (referred to as PbTe1, PbTe2, b) two n-type PbSe samples (referred to as PbSe1, PbSe2), and c) two n-type PbS (PbS1, PbS2) samples. ARPES measurements were performed using plane polarized light with 22 eV photon energy and data were collected at 2 or 4 meV energy intervals. The energy and momentum resolutions were approximately 20 meV and 0.0055 Å⁻¹, respectively. PbQ samples were prepared by melting mixtures of Pb and Q at 100–150 K above the individual melting points of Pb and Q inside evacuated fused silica tubes. PbI₂ was used for achieving n-type doping, while Na was used for p-type doping. Typical carrier concentrations of the n-type samples ranged from $2 \times 10^{19} \text{ cm}^{-3}$ to $5 \times 10^{19} \text{ cm}^{-3}$, while those of the p-type samples ranged from $0.2 \times 10^{19} \text{ cm}^{-3}$ to $2 \times 10^{19} \text{ cm}^{-3}$. These samples were cleaved in situ to expose a fresh surface (001) of the crystal for ARPES measurements.

**Results.** – In order to elucidate the ARPES data, we first consider the bulk Brillouin zone (BZ) of PbQ, which has a face centered cubic (fcc) crystalline structure. This BZ is represented in fig. 1(a). PbQ is preferentially cleaved along the (001) plane and hence, we concentrate on its square surface BZ projected onto the (001) plane. As shown in fig. 1(a), the $\Gamma$ and L points project on the ($\bar{\Gamma}$) and ($\bar{X}$) of the surface BZ. In figs. 1(b)–(g), we show constant-energy intensity maps (CEIMs), i.e., ARPES data as a function of in-plane momentum components $k_x$ and $k_y$ at fixed $\bar{\sigma}$’s, where $\bar{\sigma}$ is the electronic energy with respect to chemical potential. Figures 1(b) and (e) correspond to the CEIMs at $\bar{\sigma} = -40$ meV and $-200$ meV, respectively for a p-type PbTe sample (PbTe1). Hole pockets derived from the UVBs centered at L points are clearly visible around $\bar{X}$ at $\bar{\sigma} = -40$ meV (fig. 1(b)), while tubular regions connecting these isolated pockets appear at $\bar{\sigma} = -200$ meV (fig. 1(e)). First-principles calculations [29,32,33] predict that, such tubular regions are associated with the presence of secondary valence bands, i.e., the LVBs. Figures 1(c) and (d) show the CEIMs of the n-type PbSe and PbS samples, respectively, at $\bar{\sigma}$’s close to the top of their UVBs. Similarly, figs. 1(f) and (g) correspond to the CEIMs of the n-type PbSe and PbS samples, respectively, at $\bar{\sigma}$’s close to the top of their LVBs. As can be seen from fig. 2, the UVBs as well as the LVBs of the n-type samples lie deeper in energy compared to those of the p-type sample. Therefore, the $\bar{\sigma}$’s of the CEIMs of the n-type samples are more negative compared to those of the p-type sample. Nevertheless, the evolution of the CEIMs with $\bar{\sigma}$’s appears to be qualitatively similar in all three samples. The method for constructing the CEIMs in fig. 1 is as follows: starting from the raw ARPES data, we first subtract the constant signal at $\bar{\sigma} > 0$ (due to second-order light) and then, we normalize each ARPES spectrum by the area enclosed by it and the energy axis between measured values of $\bar{\sigma}$. The raw data covered more than one half of the surface BZ for each sample. For better visualization, the CEIMs in the entire BZ were reconstructed by reflections, using interpolations to uniform grids.

To further investigate the valence band structure of PbQ, we look into fig. 2. Here band dispersions and ARPES energy-momentum intensity maps (EMIMs) along two specific momentum space cuts, namely cut 1 and cut 2 defined in fig. 1, are presented. Figures 2(b), (f), (j) correspond to EMIMs along cut 1, while figs. 2(d), (h), (l) to those along cut 2. Figures 2(b), (d) correspond to a n-type PbS sample, figs. 2(f), (h) to a n-type PbSe, and figs. 2(j), (l) to a p-type PbTe sample. One can recognize an electron band, i.e., the conduction band (CB), separated in energy and momentum from a hole band, i.e., the UBV, in EMIMs along cut 1 for n-type PbS and PbSe samples. The CB of the p-type PbTe sample is invisible as it is in the unoccupied side. On the contrary, a separate hole band alone is present along cut 2 in each of figs. 2(d), (h), (l). As to the first-principles calculations, the secondary valence band maxima are located away from $\Gamma$-$Y$-$X$ where the fundamental gap is found so that the next maxima would correspond to the LVB. Therefore, we identify the hole bands along cut 2 as the so-called LVBs since their maxima are located away from $\bar{\Gamma}$-$\bar{X}$. We would like to point out that all high-symmetry lines including
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\[ \Gamma - X, \Gamma - K, K - W \text{ and } W - X \text{ project onto } \Gamma - M \text{ in the (100) surface Brillouin zone. It will be an important topic for future studies to establish the association of this second valence band to a specific bulk electronic state via a detailed study of the three-dimensional electronic structures. Nevertheless, figs. 1 and 2 together corroborate the two-band picture for the valence band structure of PbQ.} \]

Now we discuss how to extract the band edge at a specific momentum location of the CBs, UVBs and LVBs of PbQ. In figs. 2(n) and (o), we plot energy distribution curves (EDCs) along with their second derivatives with respect to \( \vec{\Omega} \) at \( k^U \) and \( k^L \), respectively, for a PbS sample. In this context, an EDC is the distribution of electrons as a function of \( \vec{\Omega} \) at a fixed momentum, while \( k^U \) and \( k^L \) are the momentum location of the band maximum (BM) of the UVB and LVB, respectively. On closer inspection, fig. 2(n) reveals a rather sharp rise in intensity of the EDC on top of a nearly flat background signal below a certain value of \( \vec{\Omega} \). We define this particular \( \vec{\Omega} \) as \( \Omega_U \), which is the band edge of the UVB at \( k^U \). The intensity of the EDC in fig. 2(n) also exhibits similar abrupt increase above a certain value of \( \vec{\Omega} \). We call this \( \vec{\Omega} \) as \( \Omega_L \), which denotes the band edge of the CB at \( k^L \).

**Fig. 2:** (Colour online) Band dispersions (shown by open circles) and EMIMs along cut 1 for ((a), (b)) PbS, ((e), (f)) PbSe and ((i), (j)) PbTe, and along cut 2 for ((c), (d)) PbS, ((g), (h)) PbSe and ((k), (l)) PbTe. Parabolic fittings of the dispersions are shown by solid curves in (a), (c), (e), (g), (i), and (k).

The positions of \( \Omega_U \) and \( \Omega_L \) agree well with the peak positions of the second derivative of the EDC. (o) EDC (magenta curve) and its second derivative (golden curve) at \( k^L \) for PbS. The blue line through data points in (n) guides almost linearly increasing intensity of the EDC with \( \vec{\Omega} \), while the green line for \( \vec{\Omega} > \Omega_C \). The positions of \( \Omega_U \) and \( \Omega_C \) agree well with the peak positions of the second derivative of the EDC. (o) EDC (magenta curve) and its second derivative (golden curve) at \( k^L \). The black line through data points shows the linear increase in intensity of the EDC with \( \vec{\Omega} \) for \( \vec{\Omega} < \Omega_U \). The position of \( \Omega_U \) also matches nicely with the peak position of the second derivative of the EDC. \( k_1 = k_x - (k^U)_x, k_2 = k \cdot \hat{\epsilon} - k^L \cdot \hat{\epsilon} \), where \( \hat{\epsilon} \) is the unit vector along the momentum space cut 2.

The band edge of the LVB at \( k^L \), can be obtained by utilizing identical analysis of the EDC at \( k^L \), as shown in fig. 2(o). \( \Omega_U \) and \( \Omega_L \) define the momentum locations of the BM of the UVB and the LVB, respectively, while \( \Omega_L \) that of BB of the CB (fig. 2(m)). It is also evident that \( \Omega_U \), \( \Omega_C \) and \( \Omega_L \) also correspond to the local maxima of the second derivatives of the relevant EDCs with respect to \( \vec{\Omega} \).

This is demonstrated via figs. 2(n), (o) and further elaborated in figs. S1 and S2 of the supplementary material Supplementary material.pdf (SM).

One can track the maxima of the second derivative with respect to \( \vec{\Omega} \) of the EDCs at various momentum locations along a band, which, in turn, corresponds to the momentum profile of its band edges. Such momentum profile of the band edges, as can be seen from figs. 2 and S2, has the same shape as the band itself and thus, can be used for evaluating effective mass of the band. Constructed via the above-described second derivative analysis, band dispersions of the UVBs are presented in figs. 2(a), (e), (i), while those of LVBs are plotted in figs. 2(c), (g), and (k). From parabolic fitting of a dispersion in the vicinity of its BM, the corresponding effective mass can be approximated. The values of the effective masses listed in table 1.
clearly show that LVBs are heavier than UVBs in PbQ. This can readily be inferred by visual comparisons of their EMMs as well.

The band gap $\Delta_U$ of the UVB is given by $\Delta_U = \Omega_C - \Omega_U$ (fig. 2(m)). Similarly, the band gap $\Delta_L$ is $\Delta_L = \Omega_C - \Omega_L$ (fig. 2(m)). We would like to point out that these band gaps do not correspond to the gaps in the electronic band dispersions. Instead, they are the gaps in the momentum-resolved density of states. In table 2, we display $\Delta_U$ and $\Delta_L$ for various $n$-type PbQ samples. Data from PbSe and PbS are shown in fig. 2, while those from the $n$-type PbTe sample are displayed in fig. S3 of the SM. The samples under current studies do not have the exact same carrier concentration and thus, the useful quantity to be compared is $\Delta = \Delta_L - \Delta_U$, i.e., the difference between energy gaps of the LVB and UVB. Table 2 shows that $\Delta$ is largest for PbS and smallest for PbTe, while it is in between for PbSe and PbTe at $T \sim 100$ K.

The objective of the remainder of the paper is to investigate the impact of increasing $T$ on the valence bands of PbQ. This is summarized in figs. 3 and 4. In fig. 3, we plot $T$-dependent EDCs for two $p$-type PbTe ((a), (b)) and PbTe1, and (e), (f) for PbTe2), one $n$-type PbSe ((c), (d)), and one $n$-type PbS ((g), (h)) samples. The EDCs in figs. 3(a), (e), (c) and (g) are at momentum location $k^U$, while those in figs. 3(b), (f), (d) and (h) are at $k^L$. Following the procedures enunciated via fig. 2, we obtain $\Delta_U(T)$ and $\Delta_L(T)$ for both PbSe and PbS and then plot them in figs. 4(a) and (b). $\Delta_U$ depends rather weakly on $T$. In sharp contrast to this, $\Delta_U$ grows appreciably with rising $T$, which is consistent with positive temperature-derivative coefficients of the fundamental band gap found by optical experiments in PbQ [24,34–36]. It is worth mentioning that such a positive rate of change of the band gap with $T$ in PbQ is opposite to what occurs in most other semiconductors. In fact, this anomaly helps PbQ to achieve high thermoelectric efficiency since it can mitigate the bipolar effects arising from intrinsic carrier activation. The latter causes the suppression of the thermoelectric figure of merit $zT$ at high $T$’s in a material. We also point out that $\Omega_C$ of the $p$-type PbTe sample cannot be determined since its conduction band lies in the unoccupied side of its band structure. We can, however, locate $\Omega_U$ from figs. 3(a), (e) and $\Omega_L$ from figs. 3(b), (f). Therefore, $\Delta(T) = \Omega_U(T) - \Omega_L(T)$ of PbTe like PbSe or PbS can be plotted.

It is evident that $\Delta$ of each PbQ sample decreases monotonically with increasing $T$ (fig. 4(c)) in the $T$ range of our measurements. $\Delta(T)$ can be well represented by straight lines. From the linear extrapolation of $\Delta(T)$ to zero, a characteristic temperature $T^\ast$ can be defined, at which the
BM of the LVB is expected to merge with that of the UVB. The estimated values of the merging temperature $T^*$ are 813 K (PbTe), 1148 K (PbSe) and 1296 K (PbS). Although such estimation of $T^*$ involves an extrapolation over a large $T$ range, the values of $T^*$ obtained from our ARPES data agree reasonably with those from recent magnetic and optics measurements [23,24]. We provide further details concerning the connection between various attributes of our $T$-dependent measurements and those from the literature in the SM. The monotonic $T$-dependence of $\Delta$ suggests that PbQ should become semiconductors with indirect band gap for $T > T^*$, where the heavy-hole LVB rises in energy above the light-hole UVB. In this scenario, the charge transport in PbQ should be dominated by the heavy holes created due to thermal excitations as $T$ approaches $T^*$ and $\Delta(T = T^*) \sim k_B T^*$. This band convergence increases the density of states of heavier holes, and, thus, results in an enhanced Seebeck coefficient and thermoelectric power factor at higher $T$'s. All these are responsible for a superior thermoelectric performance of PbQ at elevated temperatures.

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