The recent observation of replica bands in single-layer FeSe/SrTiO$_3$ by angle-resolved photoemission spectroscopy (ARPES) has triggered intense discussions concerning the potential influence of the FeSe electrons coupling with substrate phonons on the superconducting transition temperature. Here we provide strong evidence that the replica bands observed in the single-layer FeSe/SrTiO$_3$ system and several other cases are largely due to the energy loss processes of the escaping photoelectron, resulted from the well-known strong coupling of external propagating electrons to Fuchs-Kliewer (F-K) surface phonons in ionic materials in general. The photoelectron energy loss in ARPES on single-layer FeSe/SrTiO$_3$ is calculated using the demonstrated successful semi-classical dielectric theory in describing low energy electron energy loss spectroscopy of ionic insulators. Our result shows that the observed replica bands are mostly a result of extrinsic photoelectron energy loss and not a result of the electron phonon interaction of the Fe d electrons with the substrate phonons. The strong enhancement of the superconducting transition temperature in these monolayers remains an open question.

The discovery of enhanced superconductivity with transition temperatures ($T_C$) up to $\sim$65 K in the single-layer FeSe/SrTiO$_3$ has drawn intense discussion in the condensed-matter community regarding the origin of the $T_C$ enhancement. The cross-interface electron-phonon coupling is widely regarded to play an important role in this and the acclaimed strongest evidence is the observation of “shake-off” replica bands by angle-resolved photoemission spectroscopy (ARPES) at an energy of 90-100 meV in the range of a strong optical phonon in the SrTiO$_3$ (STO) substrate. It is indeed tempting to attribute the replica bands to the coupling of FeSe electrons with STO optical phonons; however theoretical estimates of the strength of this coupling and contribution to $T_C$ find this to be at most a small contribution. In subsequent experiments, similar replica bands and enhanced superconductivity properties were observed on single-layer FeSe films grown on different substrates such as BaTiO$_3$ and rutile TiO$_2$(100). This seems to suggest a commonality and an intrinsic nature of the replica bands. However, to get narrow replica bands tracing closely the dispersion of main bands crossing the Fermi energy rather than broad “shake-off” features or kinks, one has to require the coupling to be strongly peaked at $q_\parallel = 0$. Arguments for this strong peakedness were given in references. We will show that the surface Fuchs-Kliewer (F-K) phonon coupling to the escaping photoelectron is naturally strongly peaked at $q_\parallel = 0$ and in comparison to electron energy loss spectroscopy we provide direct evidence that the replica bands are a consequence of energy loss processes of the escaping photoelectron. Our conclusions are of general importance in the interpretation of self energies in ARPES measurements in insulators or low carrier density metals.

Enlightening in the search for an explanation of the replica bands in ARPES is that replica bands at the same “shake-off” energy are observed also in bare STO surfaces exhibiting a two-dimensional electron gas (2DEG) in ARPES. Even more enlightening is the recent report by Zhang et al of strong energy loss features in high-resolution electron energy loss spectroscopy (HREELS) at the same energies as the replica bands on a single-layer FeSe/STO(001) surface as well as on the bare STO surface. The HREELS results as we will show can

FIG. 1. A comparison of the angular resolved photoemission (a) and high resolution specular reflection electron energy loss spectroscopy processes (b).
be accurately described by semi-classical dielectric theory without adjustable parameters. This provides strong evidence that these loss features are due to the strong coupling of the electron approaching and then reflecting from the surface, with the deeply penetrating F-K surface phonon modes \(15, 17\). The F-K phonons with \(q_\parallel = 0\) involve modes of the positive and negative ions opposite motion perpendicular to the surface extending deep into the bulk of ionic material \(15, 17, 21, 25\). This produces a large oscillating potential extending far outside the surface. These couple strongly with electrons moving with a component perpendicular to the surface resulting in the energy loss but little parallel momentum loss.

ARPES is one of the most direct and widely-used methods to study the energy and momentum dispersion relation and especially also the so-called real and imaginary parts of the self-energy resulting from the interaction of the electrons with each other and with bosonic degrees of freedom involving excitations like magnons, excitons and phonons \(26\). Photoemission, however, is a two-particle excitation involving the photoinduced hole and the photoelectron [Fig. 1(a)] and even if the electron-hole interaction is small the two particles each carry a self-energy due to the interaction with the rest of the system. Mostly we assume and rightly so that if the energy of the photoelectron is very high i.e., high photon energy, the interaction with the photoinduced hole can be neglected (the so-called “sudden approximation”). We also mostly assume that the interaction of the escaping photoelectron with the sample can be neglected. In this case the spectra obtained will provide direct information concerning the self-energy of the photoexcited hole. However, in the case of ionic materials with F-K phonons the huge oscillating long-range external potentials above the surface \(12, 27\) can interact strongly with the photoelectron after it escapes from the sample and travels to the analyzer.

The strong interaction of externally moving electrons have been very clearly demonstrated by the HREELS experiments on ionic material surfaces for example on ZnO surface by H. Ibach \(\text{[16]}\). The energy loss peak height sometimes can be even 50% of the zero-loss peak height when using incident energies in the same range as often occurs in the kinetic energy of emitted electrons in ARPES. In this case, the collected ARPES spectrum must be corrected for the energy loss processes of the emitted photoelectron. However, to our knowledge, this information from HREELS has not been considered and used to correct ARPES spectra generally.

In this Letter, we study the photoelectron energy loss process on the single-layer FeSe/STO(001) system due to photoelectrons interacting with the F-K phonons of STO substrate. We use the well-developed semi-classical dielectric theory to describe HREELS on STO surface which depends only on the optical constants of the material and the electron kinetic energy and propagation direction, and also describe the energy loss processes of the emitted photoelectron electron in ARPES. The optical constants are available from infrared optical spectroscopy studies of STO \(28, 29\).

ARPES involves a photon-in-electron-out process [Fig. 1(a)] and most experiments are conducted with less than 100 eV photon energy or photoelectron kinetic energy about the work function lower than the photon energy when looking at states close to the chemical potential in metals \(26\). For low energy losses as for phonons of less than 100 meV, the trajectory of the emitted photoelectron hardly changes. HREELS involves an electron-in-electron-out process [Fig. 1(b)] with the monochromatized incident electron energy usually less than 100 eV \(17\). Since in specular reflection the total path of the electron in HREELS is twice as long as in ARPES and realizing that interference terms between the loss processes for the incident and reflected electrons are small except for grazing incidence \(27\), we can safely approximate the intensity of the loss in ARPES to be \(\frac{1}{2}\) of that in HREELS for the same kinetic energy and same trajectories. This is the main concept we use in what follows.

The F-K surface optical phonon modes was firstly predicted by R. Fuchs and K. L. Kliever \(15\) to be present in ionic crystal slabs and somewhat later was detected by H. Ibach on ZnO in a HREELS study \(16\). In HREELS, the incident electron with kinetic energy generating the time-variable external electric field normal to the surface direction can interact strongly with the long-wavelength transverse optical phonon \(17, 27\). As shown in Fig.

\[\text{FIG. 2. (a) A snapshot of the instantaneous position of cation and anion displacements for a long wavelength (}q_\parallel = 0\text{) transverse optical phonon in a cut out side view of a (001) terminated rock salt structure slab. The solid lines show the equilibrium positions of the ions. Here the anions are assumed to be much lighter than the cations. (b) The experimental (at 470 K) and simulated HREELS (at 470 K and 15 K) of STO(001) terminated crystal with 6.0 eV incoming electron and incident angle } \theta = 45^\circ. \text{The inset illustrates the polar displacement in STO.}\]
infinite extending surface is independent of the distance from the surface like the static case of a polar terminated
ionic crystal (i.e. the “polar catastrophe”). The magnitude of the oscillating potential outside the surface is
proportional to the penetration depth of the ionic displacements into the bulk of the crystal which decays ex-
ponentially with $q_||$. Therefore the $q_|| = 0$ mode is by far the strongest. The huge long-range dynamic
results in the very large inelastic-scattering probability in the close to specular reflection direction in HREELLS
[10, 17, 21, 25]. Since the incident electron energy is much larger than the optical phonon energy, i.e. “fast”
imcoming electrons, classical electromagnetic theory de-
scribes the energy loss process accurately resulting in the
single-loss probability given by [17]

$$P(w) = \frac{2}{a_0 k_i \cos \theta_i w} \frac{1}{\text{Im} \left( \frac{-1}{\epsilon_b(w) + 1} \right)}$$

(1)

where $a_0$ is the Bohr radius, $k_i$ and $\theta_i$ are the wavevector and incident angle of the incoming electron relative to the
perpendicular surface direction respectively and $\epsilon_b(w)$ is
the frequency dependent bulk dielectric function. For
an isotropic material with $n$ infrared-active transverse
optical phonons, the dielectric function in the Lorentz
model is given by [17]

$$\epsilon_b(w) = \epsilon(\infty) + \sum_{k=1}^{n} \frac{Q_k w_{TO,k}^2}{w_{TO,k}^2 - w^2 - i \gamma_k w}$$

(2)

where $\epsilon(\infty)$ is the high-frequency dielectric constant, $w_{TO,k}$ the infrared-active transverse-optical phonon fre-
cquency, $Q_k$ the oscillator strength and $\gamma_k$ the damping frequency. These crystal properties can be obtained di-
rectly from the infrared optical experiments. In the case
of only one oscillator, $\text{Re}(\epsilon) = -1$ in Eq. (2) determines
the F-K phonon energy at $w_{FK} = w_{TO} \sqrt{\frac{\epsilon(0)+1}{\epsilon(\infty)+1}}$ where
$\epsilon(0)$ is the static dielectric constant [17]. The F-K phonon
energy lies between the transverse and longitudinal optical
phonon frequencies using the Lyddano-Sachs-Teller
relation $\frac{w_{TO}}{w_{FK}} = \sqrt{\frac{\epsilon(0)}{\epsilon(\infty)}}$. For large inelastic-scattering
probabilities, perturbation theory breaks down and the quantum-mechanical harmonic oscillator introduced by Lucas
and Sunjic [27, 30, 31] describes the amplitude of the multiple scatterings exhibiting a Poisson intensity
distribution in the ideal case of a sole, undamped excita-
tion at zero temperature.

HREELS spectra simulated with the semi-classical di-
electric theory including the Poisson distribution are in
very good agreement with experiments for many ionic
material surfaces [21, 23, 30, 32] and in the following we
will use this theory to simulate the energy loss process
in HREELS and ARPES experiment. Figure 2(b) shows
very intense energy-loss peaks in the HREELS measured
onto STO(001) surface at 470 K by Conard et al [24]. The
two strongest energy-loss peaks are at $\sim 59 \text{ meV (} w_{FK1} \text{)}$
and $\sim 92 \text{ meV (} w_{FK2} \text{)}$ with multiple-phonon scatterings
at $\sim 118 \text{ meV (} 2w_{FK1} \text{)}, \sim 149 \text{ meV (} w_{FK1} + w_{FK2} \text{)}$
and $\sim 184 \text{ meV (} 2w_{FK2} \text{)}. The energy gain peaks on the left
of zero energy loss is due to the interactions with the
thermal excited phonon i.e. the “anti-Stokes peak”. The
STO dielectric function given by Eq. (2) can be approxi-
mated using $\epsilon(\infty) = 5.5$ and the oscillator parameters di-
rectly obtained from the infrared optical experiment [33]–
470 K, three infrared-active transverse optical phonons
including the soft mode TO1 at $\sim 14 \text{ meV (Ti-O-Ti bending),}$
TO2 at $\sim 1.5 \text{ meV (Sr ion moving against the TiO}_6$
octahedra) and TO4 at $\sim 67 \text{ meV (the Ti-O stretching)}$
[28, 34, 35]. At low temperature, a weak infrared-active
mode due to the rotation of the neighboring oxygen oc-
thedral is included [24]. As shown in Fig. 2(b), the
simulated HREELS spectrum using the semi-classical
dielectric theory exhibits very good agreement with exper-
iment in both energy gain and loss side including also
the relative intensities. At low temperature, it is well
known that the TO1 mode in STO becomes soft dramat-
ically with a very large STO static dielectric constant but
interestingly the calculated [Fig. 2(b)] and experimental
HREELS at low temperature [20] changes little from the
470 K data aside from the gain peaks. The reason for
this small change despite the large change in the static
dielectric constant is that a large change of the oscilla-
tor strength and damping also occurs in the TO2 mode
at low temperature [33] which compensates the change
of TO1 soft mode and generates almost the same two
strong energy loss peaks at $\sim 60 \text{ meV and } \sim 90 \text{ meV at } 15 \text{ K and 470 K.}$

In the following, the photoelectron inelastic-scattering
probabilities on the single-layer FeSe/STO(001) system
will be calculated with the approximation stated at the
beginning that the electron energy loss probability in
ARPES is a half of that in specular reflection HREELS.
We consider the high resolution very clear experimental
data of the Stanford group on a well characterized single-
layer FeSe film grown on a 0.05 wt% Nb-doped STO sub-
strate. The Nb doping which is needed to prevent any
charging effects in ARPES also results in a low-density
electron gas in the STO which will result in some screen-
ing of the F-K phonon modes which will tend to decrease
the experimental replica features relative to theory done
for the insulating case. Free electrons in the substrate
can couple with the F-K phonon and result in a shift and
lower intensity [17, 32, 33]. However, the effect of the low
density of charge carriers in the Nb doped STO and the 2
dimensionality of the FeSe based electron gas is expected
to be very small. For a further discussion of the depend-
ence on the electron density we refer to Section 2 & 3
in the supplementary material [33]. The ARPES exper-
iment is performed at 20 K using 24 eV photons [3] and
a kinetic energy of the photoelectron around $\sim 19.5 \text{ eV}. $
Replica bands around the M point of the 2 Fe per unit
cell Brillouin zone are measured with the analyzer angle
θ ≈ 31° relative to the perpendicular to surface.

FeSe monolayers on STO(001) exhibit two bands crossing the Fermi energy labeled A and B and this results in two sets of replica structures. In Fig. 3(a), we display the calculated ARPES spectra using the optical parameters of STO at 15 K [29] and using the same theory as that used for the HREELS spectra but reducing the loss features by a factor of 2 and modified for the somewhat different kinetic energies and angles according to energy loss theory described above. The simulated spectra in Fig. 3(a) are shifted to make the zero-loss peak overlap with the primary A and B bands in experiment. Bottom is the summation of EELS(A) and EELS(B) compared with the experimental curve. (b) The simulated replica bands resulted from the photoelectron energy loss of A and B band. The replica band intensity ratio at different wavevectors is kept constant using the one calculated at M point since it exhibits only a small change in going from \( k_M - 0.2 \) Å\(^{-1}\) to \( k_M + 0.2 \) Å\(^{-1}\) [33]. (c) The experimental ARPES result around the M point and all parameters coming from experiment without any fitting parameter, provides very strong evidences that the replica band can be well described by photoelectron energy loss processes due to the F-K phonon in the STO substrate.

The probability of generating excitations in the energy loss process depends on the measurement geometry and the photoelectron velocity. As shown in Eq. (1), it is inversely proportional to the electron momentum perpendicular to the surface, i.e. \( k \cos(\theta) \). Although this relation is not valid for close to grazing incidence because of the strong contribution of the interference terms and the influence of image charge effects [27], the theory can be nicely tested with a photon energy dependent study or experimental measurement in different Brillouin zones [33].

The replica bands resulting from the energy loss processes of the escaping electron may also be the explanation for a number of replica bands or so-called “peak-dip-hump” structures observed in thin surface metallic capping layers on ionic substrates such as STO [3, 13, 18, 19], TiO\(_2\) [14, 30] and ZnO surface [37]. When the concentration of the free electrons is low or highly-confined in a very thin layer, its interaction with the propagating photoelectron above the surface and the F-K phonon from the substrate beneath is weak and in ARPES replica bands or “peak-dip-hump” structures can be observed because the strong interactions between the propagating photoelectrons and the F-K substrate phonons [33]. When the concentration of the free electrons is high and spatially distributed in a thicker surface layer the F-K substrate phonon couples strongly with the free electrons [17, 32] leading to very low and broad energy loss peaks which can hardly be observed in ARPES [33]. In experiment, the replica intensity is indeed observed to have strong dependence on the free electron density and its thickness on the STO surface [13, 19].

In conclusion, we have demonstrated that the photoelectron energy losses on the ionic material surface can be very significant due to the strong interactions between the propagating photoelectron and the long-wavelength F-K surface phonon, which can generate clear replica bands in ARPES experiment with the “shake-off” energy equal to the F-K phonon energy. We have provided strong evidences that the replica bands recently observed for the single-layer FeSe/STO system is largely due to the extrinsic photoelectron energy loss process. This explains the observed replica structure in detail without the need of any additional electron-phonon coupling due to the FeSe electrons interacting with substrate phonons. This does not necessarily eliminate the importance of electron phonon coupling of the d electrons in FeSe to the substrate phonons which in principle if strong could lead to small polaron formation but to do this one would need a very large q range in the coupling as in the Holstein model and this would result in kinks or very broad con-
tinuum like shake up structure in ARPES. In addition, our studies strongly suggest that corrections must be introduced when analyzing photoemission spectroscopy on ionic material surfaces. Complementing the ARPES with HREELS studies on the same systems can provide the information needed to correct for this.

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