Origin of the Electron–Phonon Interaction of Topological Semimetal Surfaces Measured with Helium Atom Scattering

Giorgio Benedek, Salvador Miret-Artés,* J. R. Manson, Adrian Ruckhofer, Wolfgang E. Ernst, and Anton Tamtögl*

ABSTRACT: He atom scattering has been demonstrated to be a sensitive probe of the electron–phonon interaction parameter $\lambda$ at metal and metal-overlayer surfaces. Here it is shown that the theory linking $\lambda$ to the thermal attenuation of atom scattering spectra (the Debye–Waller factor) can be applied to topological semimetal surfaces, such as the quasi-one-dimensional charge-density-wave system Bi(114) and the layered pnictogen chalcogenides. The electron–phonon coupling, as determined for several topological insulators belonging to the class of bismuth chalcogenides, suggests a dominant contribution of the surface quantum well states over the Dirac electrons in terms of $\lambda$.

Knowledge of the electron–phonon (e–ph) interaction at conducting surfaces and the specific role of dimensionality are of great relevance both from a fundamental point of view as well as for various applications, such as two-dimensional (2D) and quasi-1D superconductivity in nanotechnology. Similarly, the e–ph interaction plays a relevant role in other transport properties, e.g., thermoelectricity, in low-dimensional systems such as layered Bi and Sb chalcogenides and in quasi-crystalline materials which are often viewed as periodic solids in higher dimensions.

In a series of recent experimental and theoretical works, it was shown that the e–ph coupling constants for individual phonons $\lambda_{Q}$ as well as their average $\lambda$ (also known as the mass-enhancement parameter or factor) $^{5,6,14}$ can be measured directly with helium atom scattering (HAS). $^{8,9}$ In particular, the study of multilayer metallic structures $^{8,9,11}$ has shown that HAS can detect subsurface phonons as deep as those that contribute to the e–ph interaction. For example, HAS can detect phonons spanning as many as 10 atomic layers in Pb films $^{8,9}$ (known as the quantum sonar effect), thus providing the individual $\lambda_{Q}$ values for phonons which provide the dominant contributions to $\lambda$. The values of $\lambda$ are obtained directly from the temperature dependence of the HAS Debye–Waller (DW) exponent, and the interaction range can be assessed from the number of layers, $n_{TH}$, above which the measured $\lambda$ becomes thickness-independent. In that analysis, the conducting surface region of a 3D material could be viewed as a stack of (interacting) 2D electron gases (2DEGs), allowing for the simpler formalism characterizing the 2DEG. $^{10,11}$ Due to the appreciable depth explored by the e–ph interaction, the values of $\lambda$ obtained from HAS (hereafter called $\lambda_{HAS}$) generally are close to the most reliable values found in the literature, thus allowing one to assess the validity of the new method.

In this work, we investigate the specific role of dimensionality in the e–ph mass-enhancement factor $\lambda_{HAS}$ as derived from HAS. The method is shown to be particularly suitable for different classes of conducting 2D materials, such as the layered chalcogenides, topological insulators, and systems characterized by a quasi-1D free electron gas, including Bi(114). The present analysis shows that the charge density wave (CDW) transition in Bi(114), recently observed with HAS, $^{13}$ is sustained by multivalley e–ph interaction with a pronounced 1D character. In the case of topological materials, the present analysis of previous HAS data on Bi$_2$Te$_3$(111) $^{15}$ and Bi$_2$Se$_3$(111) $^{14}$ as well as new experimental data on Bi$_2$Te$_3$Se$_2$(111) indicates the overwhelming contribution to $\lambda_{HAS}$ from the surface quantum well states as compared to that of the Dirac states.

The DW factor describes the attenuation due to the thermal atomic motion of the elastically scattered intensity $I(T)$ observed at temperature $T$, with respect to the elastic intensity $I_{0}$, as follows:

$$ I(T) = I_{0} \exp(-\lambda_{HAS} T) $$

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of the corresponding rigid surface $I_0$. It is a multiplicative factor usually written as an exponential function, $\exp\{-2W(k_p, k_s, T)\}$, of the final ($k_f$) and incident ($k_i$) wavevectors of the scattered atom,

$$I(T) = I_0e^{-2W(T)}$$  \hspace{1cm} (1)

where it is implicit that all quantities in eq 1 depend on the scattering wavevectors ($k_p, k_s$). For a two-body collision model, where the incident atom directly interacts with the surface target, the DW exponent is simply expressed by $2W(k_0, k_s, T) = \langle (\Delta k \cdot \mathbf{u})^2 \rangle_T$, where $\Delta k = (k_i - k_f)$ is the scattering vector, $\mathbf{u}$ is the phonon displacement experienced by the projectile atom upon collision, and $\langle \cdots \rangle_T$ indicates a thermal average. However, atoms incident on a conducting surface with energies generally well below 100 meV are scattered exclusively by the surface free-electron density, a few ångströms away from the first atomic layer so that the exchange of energy with the phonon gas occurs only via the phonon-induced modulation of the surface free-electron gas, i.e., via the e–ph interaction. Therefore, it is logical that $2W(k_0, k_s, T)$, which originates from the integrated action of all phonons weighted by their respective Bose factors, turns out to be directly proportional, under reasonable approximations, to the mass-enhancement factor $\lambda$.

The expression of $\lambda_{\text{HAS}}$ derived in refs 10 and 15 for a 3D free-electron gas is readily extended to any dimension $d$

$$\lambda_{\text{HAS}}^{(d)} = \frac{\phi Y_d}{\langle k_F^2 \rangle} \frac{2\ln \left( e^{\phi k_F^2} / k_F^2 \right) \partial T}{k_F^2}$$  \hspace{1cm} (2)

where $r_0$ is a lattice distance ($r_0^{2} \equiv A_c$ for the surface unit cell area in 2D; $r_0^{3} \equiv V_c$, the unit cell volume in 3D), $\phi$ is the work function, $k_F$ is the Fermi wavevector, $k_c$ is the perpendicular component of the incident wave vector, $k_0$ is the Boltzmann constant, $I(T)$ is the diffraction peak intensity, and $Y_d \equiv 2^{-d} \Gamma(\frac{d}{2}) \Gamma(\frac{d}{2})$ with $\Gamma$ being the Gamma function. As mentioned above and discussed in ref 11, the 3DEG of a thick slab can be viewed as a stack of $n_{\text{sat}}$ 2DEGs, where $n_{\text{sat}}$ is the number above the one at which the HAS reflectivity becomes independent of thickness. This yields the definition $n_{\text{sat}} = e^{\phi k_F^2} / V_c$, where $k_F$ is the Fermi wavevector normal to the surface and $e^{\phi}$ is the e–ph interaction range normal to the surface, i.e., the maximum depth beneath the surface from where phonon displacements can modulate the surface charge density. Note that $n_{\text{sat}}$ is the nominal thickness of a single 2DEG.

In this way, the 2D expression of the e–ph coupling constant for a three-dimensional crystal is obtained, which is reproduced here for the special case of measurements at the specular condition:

$$\lambda_{\text{HAS}}^{(2D)} = \frac{\pi}{2n_{\text{sat}}} \alpha, \alpha = -\frac{\phi}{A_F^{1/2}} \frac{2\ln \left( e^{\phi A_F^{1/2}} / A_F^{1/2} \right)}{A_F^{1/2}}$$  \hspace{1cm} (3)
When applying eq 3, it is important to distinguish between metallic surfaces, which present to the He atoms a soft repulsive potential plus a weak long-range attractive well and layered semimetal surfaces, where the free electron gas is protected by an anion surface layer that results in a hard-wall potential plus a comparatively deep attractive van der Waals potential. In the latter case, \( k_\text{v}^2 \) needs to be corrected due to the acceleration that the He atom undergoes when entering the attractive well, before being repelled by the hard wall (Beeby correction\(^{17} \)). This is made with the substitution \( k_\text{v}^2 \rightarrow k_\text{v}^2 + 2mD/\hbar^2 \), where \( m \) is the He atom mass and \( D \) is the attractive potential depth (generally derived from He-surface bound-state resonances). In many experiments, the incident energy \( E_i \) is generally much larger than \( D \), so the Beeby correction may be neglected but not, for example, in \(^3\text{He} \) spin–echo experiments, where \( E_i \) is low and comparable to \( D \).

Low-dimensional free electron gases are often characterized by a CDW instability below a critical temperature \( T_c \) generally induced by e–ph interaction via the Fröhlich–Peierls\(^{19,20} \) or the Kelly–Fal��ov multivalley mechanism,\(^{21–23} \) the former typically applying to metal surfaces with a CDW wavevector corresponding to some nesting wavevectors between the Fermi contours and the latter more appropriate to semimetal surfaces with pocket states at the Fermi level.\(^{24} \) The phonon-induced transitions between narrow pockets (nests) realize what is meant as perfect nesting. Since He atoms scattered from a conducting surface probe the surface charge density directly, the occurrence of a CDW below \( T_c \) yields additional \( T \)-dependent diffraction peaks in the elastic scattering angular distribution at parallel wavevector transfers \( \Delta \mathbf{k} = |\Delta \mathbf{K}| \) equal or close to the nesting vectors \( Q_n \) (i.e., \( Q_n = 2k_F \) for the 1D Peierls mechanism). It should be noted that the high sensitivity of HAS permits the detection of weak surface CDWs that are difficult to detect with other methods. An interesting question is whether the temperature dependence of the CDW diffraction peaks carries additional information on the e–ph interaction which sustains the CDW transition.

When considering the temperature dependence of a diffraction peak intensity for a wavevector transfer \( \Delta \mathbf{K} \) equal to either a \( \mathbf{G} \) vector of the unreconstructed surface lattice (\( \Delta \mathbf{K} = \mathbf{G} \)) or to a CDW wavevector \( \mathbf{Q}_n \), the DW exponent also involves the longitudinal mean-square phonon displacement. For an isotropic mean-square displacement, eq 2 also can be applied to diffraction peaks by replacing \( 4k_\text{v}^2 \) with \( \Delta k_\text{v}^2 + \Delta \mathbf{K}^2 \), calculated at the actual scattering geometry at which the diffraction peak is observed. In most HAS experiments, the condition \( \Delta \mathbf{K}^2 \ll \Delta k_\text{v}^2 \) holds, so little difference is expected between the \( T \) dependence of the diffraction and specular peaks, provided \( \lambda_{\text{HAS}} \) is independent, as it should be, of the scattering channel chosen in the experiment.

There is, however, a caveat for the use of a CDW diffraction intensity \( I_{\text{CDW}}(T) \). In eq 1, it has been assumed implicitly that \( W(T) \) includes all of the temperature dependence of \( I(T) \) and that this originates exclusively from thermal vibrations. This is clearly not true for the diffraction from a surface CDW which forms below \( T_c \) from a Fermi surface instability and has the temperature-dependent population of electron states near the Fermi level according to Fermi statistics. In this case, \( I_c \) has an implicit dependence on \( T \), which generally is negligible with respect to that of \( W(T) \), except near \( T_c \) here its square root \( \sqrt{\Gamma_0} \) works as an order parameter\(^ {25,26} \) and vanishes for increasing \( T \rightarrow T_c \) as \( (1 - T/T_c)^{\beta/2} \), where \( \beta \) is the order-parameter critical exponent (typically \( \beta = 1/3 \))\(^ {22,27–29} \) while \( T_c \approx 280 \, \text{K} \) in the present case\(^ {17} \).

As a good 1DEG example, it is shown that a CDW diffraction peak also may be used to extract \( \lambda_{\text{HAS}} \) away from the critical region. The ideal \((114) \) truncation of bismuth (Figure 1) is characterized by parallel atomic rows along the \( x \equiv [110] \) direction, separated by 7.1 Å in the normal direction \( y \equiv [221] \), with a unit cell including two rows (\( b = 14.2 \, \text{Å} \)) and one atom per row (atom spacing along the rows \( a = 4.54 \, \text{Å} \)). At room temperature, the Bi(114) surface is reconstructed in a \((1 \times 2) \) fashion with three missing rows out of four so as to have one row per unit cell (\( b = 28.4 \, \text{Å} \)) and one atom per row (Figure 1a,b). The electronic structure, calculated by Wells et al.\(^ {30} \) for the \((1 \times 1) \) phase (Figure 1c, left), shows cones centered at the \( \bar{X} \) and \( \bar{Y} \) points (Figure 1c,d) at the Fermi level. Those at \( \bar{Y} \) are folded into \( \bar{Γ} \) in the \((1 \times 2) \) reconstructed phase. Both electronic structures allow for a multivalley CDW via e–ph interaction, the former with 2D character and the latter with pure 1D character due to the cone alignment along \( \Gamma X \) with \( G/2 \) spacing. HAS angular distributions along \( \Gamma X \)\(^ {12} \) (Figure 2a) show the growth of additional peaks at \( \pm G/2 \) and \( \pm 3G/2 \) below \( T \approx 280 \, \text{K} \), indicating the formation of a surface-commensurate CDW.\(^ {12} \) The associated \((2 \times 2) \) reconstruction
consists of a dimerization along the rows. The portion of the Bi(114)-(2 × 2) STM image reproduced in Figure 1b from Hofmann et al.31,32 suggests a phase correlation between rows, giving an oblique (2 × 2) unit cell and a corresponding elongated hexagonal Brillouin zone (BZ) (Figure 1d).

The HAS DW exponents for the specular G = (0, 0), diffraction G = (1, 0) and CDW (3/2, 0) peaks measured as a function of temperature below Tc are plotted in Figure 2b. The specular and diffraction DW exponents have almost the same slopes, with the small difference being compensated for by the ratio (Δkz)_{(0,0)}/[Δkz^2 + ΔK^2]_{(0,0)} resulting in the same values of λ_{HAS}^{(1D)} within less than 1%. The input data in eq 2 for d = 1 are Φ = 4.23 eV, κ = G/2 = 0.7 Å⁻¹, r(2 × 2) = 9.08 Å, incident energy Ei = 14.5 meV, and fixed scattering angle 91.5°, so (Δkz^2)_{(0,0)} = 54.3 Å⁻². The (1, 0) diffraction occurs at the incident angle of 51.2°, which gives (Δkz^2)_{(1,0)} = 53.8 Å⁻², and the resulting e-ph coupling constant is λ_{HAS} = 0.45 ± 0.03, being the same value for both specular and diffractive channels.

The CDW (3/2, 0) peak intensity (Figure 2b) shows the expected critical behavior with β ≈ 1/3, so that a value of λ_{HAS}^{(1D)} can be estimated only from the slope at the lowest temperatures. This is smaller than that for the specular peak by ≈5% and is compensated for approximately the same amount by the correcting factor (Δkz^2)_{(0,0)}/[Δkz^2 + ΔK^2]_{(3/2,0)} = 1.047, with the incident angle for the CDW peak at (3/2, 0) being 62.75°. Thus, it is reasonable to conclude that consistent values of λ_{HAS}^{(1D)} can be extracted from the T dependence of the CDW peaks.

It is interesting to compare the value λ_{HAS}^{(1D)} = 0.45 for Bi(114) to that previously derived for Bi(111), either treated as a 3D system where λ_{HAS}^{(3D)} = 0.57,10 in agreement with the value of λ = 0.60 in Hofmann’s review,14 or as a 2D system with n = 2 (a single bilayer), where it is found that λ_{HAS}^{(2D)} = 0.40, in fair agreement with a recent ab initio calculation by Ortigoza et al. for Bi(111)33 which yielded λ = 0.45, as just found here for Bi(114). As seen in Figure 2c), the DW exponent has about the same slope for Bi(114) and Bi(111), when it is divided by k_{fl}^2, in order to account for the different incident energies used in HAS experiments. The fact that λ_{HAS}^{(1D)} [Bi(114)] < λ_{HAS}^{(1D)} [Bi(111)] reflects the dimensionality effect of γ, the prefactor of eq 2. Incidentally, we note that treating the Bi(114) as a 2D system would yield a 5-fold smaller, probably unphysical, value for λ_{HAS} due to the large surface unit cell area.

Layered chalcogenides, such as 2D topological materials, with strong intralayer and weak interlayer forces form a wide class of quasi-2D materials with a conducting surface. Some transition-metal dichalcogenides (TMDC) have been investigated with HAS since the late 1980s in connection with CDW transitions, related Kohn anomalies in the bulk, and surface phonon dispersion curves.35–50 More recently, HAS studies have been extended to the surfaces of other TMDCs such as 2H-MoS2(0001)39 and 1T-PTe2 40 as well as to pnictogen chalcogenides with surface topological electronic bands at the Fermi level, such as Bi2Te3.13,41,42 and Bi2Se3.14,43

The 2D expression for the e-ph coupling constant λ_{HAS}^{(2D)} in eq 3 is the one to be used for these systems. When dealing with the e-ph coupling constant λ_{HAS} expressed as an average over the whole phonon spectrum and over all electronic transitions across the Fermi level, natural questions are (a) which phonons contribute most and (b) which electronic states at the Fermi level are more important.

The theoretical analysis by Heid et al.37 of the mode-selected e-ph coupling constants λ_{Qs} shows that in pnictogen chalcogenides, optical phonons give the major contribution to the e-ph interaction and therefore to the DW exponent. Both Bi2Se3(111)14 and Bi2Te3(111)32 exhibit two highly dispersed optical branches with deep minima at Γ for third-layer longitudinal polarization and at ~ΓM/2 for (mostly) third-layer shear-vertical (SV3) polarization. Their optical character and largest amplitude at the central chalcogen layer of the quintuple layer endow these modes with dipolar character and therefore a large e-ph interaction is consistent with Heid et al.’s theoretical analysis.47 Spin–echo 3He scattering data from Bi2Te3(111)42 suggest a Kohn anomaly also in the longitudinal acoustic branch corresponding to a nesting across the Dirac cone above the surface conduction-band minimum. As discussed in ref 47, the interband e-ph coupling occurring when the Fermi level is above the surface conduction-band minimum is enhanced largely by the involvement of surface quantum-well states. This conclusion is confirmed by the following analysis of λ_{HAS}^{(2D)} in Bi chalcogenides as a function of the Fermi-level position.

The temperature dependence of HAS specular reflectivity from the three Bi chalcogenide surfaces Bi2Se3(111), Bi2Te3(111), and Bi2Te3–Se(111) (phase II with x ≈ 1,49,40 hereafter approximated by Bi2Te3Se111) has been measured for three samples whose surface electronic states near the Fermi level, in particular, the topological Dirac states and the quantum-well states above the surface conduction-band minimum, are known from angle-resolved photoemission spectroscopy (ARPES) data.44–46,50 As seen in Figure 3 (top panel), the binding energy of the Dirac point (D) with respect to the Fermi energy E_F decreases in the sequence Bi2Se3(111) > Bi2Te3(111) > Bi2Te3Se111, as does the surface conduction-band minimum (from 0.15 to 0.08 eV and ≈0, respectively). Correspondingly, the DW exponent slope derived from the HAS specular intensity as a function of temperature also decreases. A similar behavior is expected for the e-ph coupling constant λ_{HAS}^{(2D)}, which is shown in Table 1. The latter is derived from eq 3 by setting n_{sat} = 2λ_{TF}/c0, where c0 is the quintuple layer (QL) thickness and λ_{TF} is the Thomas–Fermi screening length, accounting for the surface band-bending extension in degenerate semiconductors and semimetals.51 The factor of 2 in the above expression of n_{sat} accounts for the fact that each QL contains two metal (Bi) layers. Note that the Fermi-level density of states includes the factor of 2 for spin multiplicity, and this is appropriate for the quantum-well states above the surface conduction-band minimum that mostly contribute to λ_{HAS}^{(2D)}. On the other hand, no factor of 2 in n_{sat} is necessary when only the Dirac states are involved, due to their multiplicity of 1. The uncertainties (±) given for λ_{HAS} in the following text are based on the confidence bounds of the DW slope. Other sources in terms of the uncertainty are A_x, Φ, and λ_{TF} with the largest contribution likely to be due to λ_{TF}. Taken together, it is safe to assume a relative uncertainty of about 10% for λ_{HAS} in the first column). This clearly indicates the dominant role of surface quantum-well (QW) states over the modest contribution of Dirac electrons. The enhancement effect of QW states and related interband transitions has been investigated...
Relative Uncertainty of about 10%) in Comparison with Values from Other Sources.

Bi2Te3(111) by Heid et al.47 As shown by Pan et al.,60 in Bi2Te3(111), and theoretically for Bi 2Se3(111) and λ order of coupling constant turns out to be quite small, ranging from

\( \lambda \) level is less than 0.3 eV above the Dirac point, the e

HAS in Bi2Te2Se(111) under similar conditions. The experimental data in this work was obtained on the HAS apparatus in Cambridge. 18 In both cases, the scattering

Corresponding e−ph coupling constants \( \lambda_{\text{HAS}} \) decrease from Bi2Se3(111) to Bi2Te2Se(111), suggesting a dominant role in the e−ph interaction of the conduction band quantum-well electronic states over the Dirac electrons.

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Figure 3. Three different Bi chalcogenides Bi2Se\(_x\) Bi2Te\(_x\) and Bi2Te2Se: (a) ARPES data for the (111) surface of three Bi chalcogenides with decreasing binding energy of the Dirac point (D) and of the surface conduction-band minimum (from 0.15 eV in Bi2Se\(_x\) (reproduced with permission, copyright 2012 by the Institute of Physics) to 0.08 eV in Bi2Te\(_x\) (reproduced with permission, copyright 2014 by the American Physical Society) and ≤0 in Bi2Te2Se (reproduced with permission, copyright 2014 by the American Chemical Society). (b) DW exponent slopes from HAS specular intensity measured as functions of temperature with the scattering plane in the \( \Gamma \text{M} \) direction for the same samples. Corresponding e−ph coupling constants \( \lambda_{\text{HAS}} \) decrease from Bi2Se3(111) to Bi2Te2Se(111), suggesting a dominant role in the e−ph interaction of the conduction band quantum-well electronic states over the Dirac electrons.

Table 1. Input Data for the Calculation from the HAS DW Exponent and Results for the e−ph Coupling Constant \( \lambda_{\text{HAS}}^{(2D)} \) (with a Relative Uncertainty of about 10%) in Comparison with Values from Other Sources

| Surface          | \( k_x \) [Å\(^{-1}\)] | \( \phi \) [eV] | \( \lambda_{\text{TF}} \) [Å] | \( \Lambda_{\text{D}} \) [Å] | \( \phi_{\text{HH}} \) [Å] | \( D \) [meV] | \( \lambda_{\text{HAS}}^{(2D)} \) | \( \lambda \) (other refs) |
|------------------|----------------------|----------------|------------------|------------------|------------------|----------------|----------------|------------------|
| Bi2Se3(111)      | 10.1\(^{14}\)        | 4.9\(^{15}\)   | 0.1\(^{60}\)     | 14.92            | 9.60             | 6.54\(^{16}\)  | 0.23           | 0.17, 0.52       |
| Bi2Te3(111)      | 9.9\(^{15}\)         | 4.9\(^{15}\)   | 0.1\(^{10}\)     | 16.46            | 10.16            | 6.22\(^{10}\)  | 0.19           | 0.19, 0.52       |
| Bi2Te2Se(111)    | 10.7\(^{14}\)        | 4.9\(^{15}\)   | 0.1\(^{70}\)     | 16.09            | 10.0             | 6.4\(^{15}\)   | 0.08           | 0.12, 0.52       |

\( ^{a} \)This work. \( ^{b} \)Average over Bi2Se3(111) and Bi2Te3(111).

In conclusion, it has been shown that the temperature dependence of HAS specular reflectivity allows for the determination of the electron−phonon coupling constant of topological semimetal surfaces. In the case of the quasi-1D Bi(114) surface, the DW factor from the CDW diffraction peak yields an e−ph coupling constant \( \lambda_{\text{HAS}}^{(2D)} \) consistent with that derived from the reflectivity. Therefore, the e−ph interaction acts as the driving mechanism for the observed multivalley CDW transition. In the absence of spin−orbit coupling, the phonon angular momentum cannot convert to an electron spin-flip, so no good nesting would be allowed across the Dirac cone and only the strong spin−orbit coupling occurring in topological materials allows for a comparatively weak e−ph intracone interaction. The multivalley mechanism at the zone boundary overcomes the nesting problem because with more Dirac cones separated by less than a G vector there is always a good intercone (i.e., multivalley) nesting, even for opposite chiralities. Such a favorable circumstance, allowing for a substantial \( \lambda_{\text{HAS}}^{(2D)} \) in Bi(114) and a CDW transition, does not occur in pnictogen chalcogenides due to the single Dirac cone location in the center of the BZ. Most of their appreciable e−ph interaction is provided by the QW states, as long as they are located at the Fermi level. The present extension of HAS analysis from metal surfaces\(^{9,10}\) and thin metal films\(^{11}\) to topological semimetal surfaces qualifies He atom scattering as a universal tool for the measurement of electron−phonon coupling in conducting low-dimensional systems.

### Experimental Methods

The experimental data in this work was obtained on the HAS apparatus in Graz\(^{61}\) and the \( ^{3} \)He spin−echo scattering apparatus in Cambridge. 18 In both cases, the scattering intensity of a nearly monochromatic He beam in the range thoroughly by Chen et al.\(^{52}\) with high-resolution ARPES for the family Bi2Te\(_x\)Se\(_x\)(111) (0 ≤ \( x \) ≤ 3), including n-type Bi2Te\(_x\)(111), and theoretically for Bi2Se3(111) and Bi2Te3(111) by Heid et al.\(^{47}\) As shown by Pan et al.,\(^{60}\) in accurate ARPES studies on bulk Bi2Se3(111) samples, where only Dirac topological states are involved because the Fermi level is less than 0.3 eV above the Dirac point, the e−ph coupling constant turns out to be quite small, ranging from 0.076 ± 0.007 to 0.088 ± 0.009, similar to that found with HAS in Bi2Te2Se(111) under similar conditions.

Since the surface QW states extend into the bulk on the order of \( \lambda_{\text{TF}} \), i.e., much longer than the penetration of surface Dirac states, it is interesting to compare the above results for \( \lambda_{\text{HAS}}^{(2D)} \) with the corresponding values of \( \lambda_{\text{HAS}}^{(1D)} \) when these materials are treated as 3D materials. The ratio \( \lambda_{\text{HAS}}^{(1D)}/\lambda_{\text{HAS}}^{(2D)} \approx \pi/(k_x \lambda_{\text{TF}}) \), with \( k_x \approx 0.1 \text{ Å}^{-1} \) (Figure 3, top) and \( \lambda_{\text{TF}} \) representing the 3DEG thickness, turns out to be \( \approx 1 \).

Unlike Bi(114), where the quasi-1D character of the electron gas is quite evident, in layered pnictogen chalcogenides the considerable penetration of the QW states gives \( \lambda_{\text{HAS}}^{(2D)} \approx \lambda_{\text{HAS}}^{(1D)} \). This is consistent with the fact that the QW states are the surface states which provide the major contribution to the e−ph interaction. Information about which phonons contribute most to \( \lambda \) can also be obtained from inelastic HAS intensities, as explained in the introduction. The Kohn anomalies reported in the lower part of the phonon spectrum\(^{41−43}\) are indicative of a strong e−ph coupling for specific wavevectors and frequencies, though it has been predicted that the major contribution in these materials comes from polar optical modes.\(^{47}\) Indeed, this is in agreement with recent HAS measurements of the phonon dispersion curves in Bi2Se3(111),\(^{14}\) which indicate the longitudinal optical branch L3 (with the largest displacement on the third (Se) atomic plane) as the one having the largest mode-selective e−ph coupling.

Table 1. Input Data for the Calculation from the HAS DW Exponent and Results for the e−ph Coupling Constant \( \lambda_{\text{HAS}}^{(2D)} \) (with a Relative Uncertainty of about 10%) in Comparison with Values from Other Sources

| Surface          | \( k_x \) [Å\(^{-1}\)] | \( \phi \) [eV] | \( \lambda_{\text{TF}} \) [Å] | \( \Lambda_{\text{D}} \) [Å] | \( \phi_{\text{HH}} \) [Å] | \( D \) [meV] | \( \lambda_{\text{HAS}}^{(2D)} \) | \( \lambda \) (other refs) |
|------------------|----------------------|----------------|------------------|------------------|------------------|----------------|----------------|------------------|
| Bi2Se3(111)      | 10.1\(^{14}\)        | 4.9\(^{15}\)   | 0.1\(^{60}\)     | 14.92            | 9.60             | 6.54\(^{16}\)  | 0.23           | 0.17, 0.52       |
| Bi2Te3(111)      | 9.9\(^{15}\)         | 4.9\(^{15}\)   | 0.1\(^{10}\)     | 16.46            | 10.16            | 6.22\(^{10}\)  | 0.19           | 0.19, 0.52       |
| Bi2Te2Se(111)    | 10.7\(^{14}\)        | 4.9\(^{15}\)   | 0.1\(^{70}\)     | 16.09            | 10.0             | 6.4\(^{15}\)   | 0.08           | 0.12, 0.52       |

\( ^{a} \)This work. \( ^{b} \)Average over Bi2Se3(111) and Bi2Te3(111).
of 8–15 meV is monitored as a function of incident angle \( \theta \) and at various surface temperatures. The DW measurement of Bi$_2$Te$_3$ can be found in ref 13, while the DW data of Bi$_2$Se$_3$ is reported in ref 14. Most of the Bi(114) data has been published in the work of Hofmann et al., whereas the Bi$_2$Te$_3$Se experimental data is presented here for the first time.

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**Notes**
The authors declare no competing financial interest.

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