

The Electron–Phonon Interaction of Low-Dimensional and Multi-Dimensional Materials from He Atom Scattering

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Atom scattering is becoming recognized as a sensitive probe of the electron–phonon interaction parameter λ at metal and metal-overlayer surfaces. Here, the theory is developed, linking λ to the thermal attenuation of atom scattering spectra (in particular, the Debye–Waller factor), to conducting materials of different dimensions, from quasi-1D systems such as W(110):H(1 × 1) and Bi(114), to quasi-2D layered chalcogenides, and high-dimensional surfaces such as quasicrystalline 2ML-Ba(0001)/Cu(001) and d-AlNiCo(00001). Values of λ obtained using He atoms compare favorably with known values for the bulk materials. The corresponding analysis indicates in addition, the number of layers contributing to the electron–phonon interaction, which is measured in an atom surface collision.

The electron–phonon (e–ph) interaction at conducting surfaces together with its dimensionality are of great importance both at fundamental and technological levels. The discovery of superconductivity in 2D films dates back over 80 years.^[1,2] Initially, these were 2D metallic films deposited on inert substrates,^[1] but in recent times more exotic 2D systems have exhibited superconducting properties, such as the surface of topological insulators or twisted bilayer graphene. The theoretical explanation of the mechanisms involved in these surface systems is not clear, and even the role of electron correlations versus the e–ph interaction is not clear.^[2] One parameter that has proven to be useful in describing conventional superconductivity in the bulk

is the e–ph coupling constant λ . Here we show that the e–ph coupling constant can be measured in the surface region with He atom scattering experiments, thus enabling a measurement of this useful parameter specific to the 2D surface region.

Very recently, the e–ph interaction has been shown to play a relevant role in topological semimetal surfaces such the quasi-1D charge density wave system Bi(114) and the layered pnictogen chalcogenides.^[3] The e–ph coupling in these materials for individual phonons $\lambda_{\mathbf{Q},\nu}$ (where $\mathbf{Q}$ denotes the surface parallel wave vector and ν the branch number), and its average λ , the well-known mass-enhancement factor^[4–6]

can be directly measured with supersonic Helium atom scattering (HAS).^[7–11] With this experimental technique, subsurface phonons were detected on multilayer metallic structures^[7,10] exploring the fairly long range of the e–ph interaction, for example, spanning as many as ten atomic layers in Pb films^[7,8] (known as the quantum sonar effect). Under reasonable approximations, from the thermal attenuation of the diffraction peaks ruled by the so-called Debye–Waller (DW) factor as well as the interaction range through the number of layers n_{sat} , λ_{HAS} values can actually be extracted which agree fairly well with previous values for the bulk or obtained from other surface techniques.^[3,9,10] This quantity n_{sat} indicates the number of layers above which the measured λ becomes thickness-independent.

In this work we focus on the specific role of dimensionality in the e–ph mass-enhancement factor as derived from HAS.^[3] In particular, we extract λ_{HAS} values from HAS data for different classes of conducting surfaces characterized by nearly free-electron gases of growing dimensions, from the quasi-1D systems such as W(110):(1 × 1)H and Bi(114), and the quasi-2D layered chalcogenides, to quasicrystalline surfaces such as the dodecagonal 2ML-Ba(0001)/Cu(001) and decagonal d-AlNiCo(00001), which can be regarded as behaving like periodic 4D and 5D materials, respectively.

As is well known, the DW factor describes the thermal attenuation, due to the surface atomic motion, of the elastic scattered intensity $I(T)$ observed at temperature T with respect to the elastic intensity of the corresponding rigid surface I_0 . It is usually written as

$$I(T) = I_0 e^{-2W(T)} \quad (1)$$

where the DW factor, $\exp\{-2W(\mathbf{k}_f, \mathbf{k}_i, T)\}$, depends explicitly on the final ($\mathbf{k}_f$) and incident ($\mathbf{k}_i$) wave vectors of the scattered atom. When zero point motion vibrations can be neglected,

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which holds for T comparable to or larger than the surface Debye temperature of the material, the argument of the exponential, $2W(T)$, is approximately linear in T .

When the incident atom directly interacts with the surface, the DW exponent is simply expressed by $2W(\mathbf{k}_f, \mathbf{k}_i, T) = \langle (\Delta \mathbf{k} \cdot \mathbf{u})^2 \rangle_T$, $\Delta \mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ being the scattering vector, $\mathbf{u}$ the phonon displacement experienced by the projectile atom upon collision, and $\langle \dots \rangle_T$ means a thermal average. For energies typically well below 100 meV, incident atoms are exclusively scattered by the surface free-electron density, a few Å away from the first atomic layer. Thus, the exchange of energy with the phonon gas mainly occurs via the phonon-induced modulation of the surface free-electron gas or the so-called e-ph interaction. Under reasonable approximations, it has been recently shown that the DW exponent is proportional to λ and in the simplest case reads as^[9]

$$2W(\mathbf{k}_f, \mathbf{k}_i, T) \equiv 4\mathcal{N}(E_F) \frac{mE_{iz}}{m_e^* \phi} \lambda k_B T \quad (2)$$

where $\mathcal{N}(E_F)$ is the electron density of states at the Fermi energy E_F , m and m_e^* are the projectile atomic mass and the electron effective mass, respectively, ϕ is the work function and k_B is the Boltzmann constant. Equation (2) is written here specifically for the specular diffraction peak for which $E_{iz} = E_i \cos^2(\theta_i) = \hbar^2 k_{iz}^2 / 2m$ is the incident energy associated with the motion normal to the surface for the given incident angle θ_i . For application to non-specular diffraction peaks or to other elastic features, Equation (2) needs to be adjusted to account for the correct scattering vector appropriate to the scattering configuration, that is, $4k_{iz}^2 \rightarrow \Delta k^2 = (\mathbf{k}_f - \mathbf{k}_i)^2$ as discussed below. Using the simple expression of Equation (2), a previous analysis of the thermal attenuation of the specular peaks of He atom scattering from several simple metals extracted values of λ_{HAS} .^[9] These values must be regarded as values of the electron-phonon constant relevant to the region near the surface.

An important observation concerning the DW factor $2W(\mathbf{k}_f, \mathbf{k}_i, T)$ is that it is rigorously proportional to the temperature, subject to the condition that T is large compared to the Debye temperature (which in practice means that T should be larger than about half the Debye temperature). This results because the average phonon mean-square displacement satisfies similar conditions as long as the crystal obeys the harmonic approximation. Thus, plots of $2W(\mathbf{k}_f, \mathbf{k}_i, T)$ versus T (usually called DW plots) have linear slopes at large T , although at small values of T where zero point motion becomes effective the curve saturates to a constant value.

There have been extensive He atom scattering measurements of successive layers of alkali metals grown on various metal substrates, and similar studies of multiple Pb layers grown on Cu(111).^[10] These systems are of interest for studies of the e-ph constants, for example, to see how λ_{HAS} varies as a function of numbers of monolayers. The case of multiple Pb monolayers is of particular interest because thin films of Pb on Si and GaAs are known to remain superconductors down to one monolayer.^[7,12–15] An interesting first observation of the thermal attenuation of specular He atom scattering for layer-by-layer growth is that, for a given system, the slope of the DW plots increased linearly with

layer number n for the first few layers up to a saturation number n_{sat} which was typically about five layers.^[10] This behavior suggests that each layer of these simple metals contributes similarly and additively to the Fermi level density of states appearing in Equation (2), a property which is also indicated by theoretical calculations for multi-layer alkali films.^[16] For the surface of bulk simple metals, using for the Fermi level density of states that of a 3D free electron gas, $\mathcal{N}(E_F) = 3Zm_e^* / \hbar^2 k_F^2$, where k_F is the Fermi wave vector and Z the number of free electrons per atom, was a satisfactory approximation.^[10] However, the linearly increasing slope observed for ultrathin films with $n < n_{sat}$ suggests that it is appropriate to attribute to each metal layer an independent contribution of the 2D free electron density of states (DOS), which implies that $\mathcal{N}(E_F) = nm_e^* a_c / \pi \hbar^2$ for $n \leq n_{sat}$ where a_c is the area of the surface unit cell. Combining this last expression (2D form) for the Fermi level density of states, and recognizing that $\ln[I(T)/I_0] = -2W$, the following expression for λ from Equation (2) is obtained

$$\lambda_{HAS} = \frac{\pi}{2n} \alpha; \alpha \equiv \frac{\phi \ln[I(T_1)/I(T_2)]}{a_c k_{iz}^2 k_B (T_2 - T_1)}, \text{ for } n \leq n_{sat} \quad (3)$$

where T_1 and T_2 are any two temperatures in the linear region of the DW plot. If n_{sat} is known one can use the 2D expression for $n > n_{sat}$ by setting $n = n_{sat}$ (this is what has been done for all layered crystals); alternatively, the 3D expression can be used. Interestingly, Equation (3) is written in a form in which the factor of $1/n$ is cancelled out by the linear increase in n of $\ln[I(T_1)/I(T_2)]$ resulting in a value of λ_{HAS} that is essentially independent of the monolayer number n , even for $n > n_{sat}$ where the 3D Fermi density of states is applied. Analysis of the data for thermal attenuation of the specular He atom diffraction peak for up to ten layers of the alkali metals Li, Na, K, Rb, and Cs deposited on various metal substrates produced values for λ_{HAS} that are in quite reasonable agreement with known tabulated values for bulk crystals, and similarly for up to 25 ML of Pb deposited on Cu(111).^[10]

The success of the theory expressed in Equations (2) and (3) in obtaining values of λ_{HAS} in systems of layer-by-layer growth leads naturally to the question of applying similar theory to obtain λ for other types of layered compounds. In particular, there are several chalcogenide compounds for which DW attenuation measurements of He atom diffraction have been reported. We show below that with appropriate interpretation of Equations (2) and (3) reliable values of λ_{HAS} can be extracted from such experimental data.

Dimensionality^[17] enters the expression of λ_{HAS} through the Fermi-level DOS per unit energy $\mathcal{N}_F^{(d)}$ and unit d -dimensional hyper-volume

$$\mathcal{N}_F^{(d)} = \frac{k_F^d}{\gamma_d E_F} \quad (4)$$

where

$$\gamma_d \equiv 2^{d-1} \pi^{d/2} \Gamma\left(\frac{d}{2}\right) \quad (5)$$

d being the dimension, and Γ the Riemann gamma-function, which for integer d has values given by

$$\Gamma\left(\frac{d}{2}\right) = \left(\frac{d}{2} - 1\right)!; \quad d \text{ even} \quad (6)$$

$$= \frac{(d-2)!!\sqrt{\pi}}{2^{(d-1)/2}}; \quad d \text{ odd.}$$

For $d = 2$, $\gamma_2 = 2\pi$, and $d = 3$, $\gamma_3 = 2\pi^2$, the usual 2D electron gas (2DEG) and 3D electron gas (3DEG) expressions, namely $\mathcal{N}_F^{(2)} = m_e^*/\pi\hbar^2$ and $\mathcal{N}_F^{(3)} = m_e^*k_F/\pi^2\hbar^2$, respectively, are readily obtained with $k_F = (2m_e^*E_F)^{1/2}/\hbar$. As discussed elsewhere,^[10] the 3DEG of a thick anisotropic degenerate semiconductor slab can be viewed as a stack of a number $n = n_{\text{sat}}$ of 2DEGs. This yields a definition of n_{sat} as

$$n_{\text{sat}} = c^* \frac{k_F}{\pi} \quad (7)$$

where c^* has the meaning of the e-ph interaction range normal to the surface or the maximum depth beneath the surface from where phonon displacements can modulate the surface charge density. In this way, the 2D expression for the e-ph coupling constant for a thick layer crystal as given in ref. [10] is just that of Equation(3) with $n = n_{\text{sat}}$.

For a general d -dimensional free-electron system (for any d , even fractional), one finds

$$\lambda_{\text{HAS}}^{(d)} = -\frac{\phi\gamma_d}{4(k_F r_0)^d} \frac{k_F^2}{k_{iz}^2} \frac{\partial \ln\{I(T)\}}{k_B \partial T} \quad (8)$$

where r_0^d is the unit cell hyper-volume. Similarly, in the case of a measurement of the dependence on the HAS specular reflectivity as a function of the incident wave vector at constant T , the expression for $\lambda_{\text{HAS}}^{(d)}$ becomes^[11]

$$\lambda_{\text{HAS}}^{(d)} = -\frac{\phi\gamma_d}{4(k_F r_0)^d} \frac{k_F^2}{k_B T} \frac{\partial \ln\{k_i^\eta I(T)\}}{\partial (k_{iz}^2)} \quad (9)$$

The factor of k_i^η multiplying the intensity is a correction for the energy dependence of the incident beam flux. The standard theoretical treatment of a jet beam nozzle expansion flow shows that the beam energy varies inversely as the square root of the stagnation temperature. The correction factor is then simply k_i , or $\eta = 1$,^[18] although in some cases different behaviors on incident energy have been measured. Further discussion on the dependence of the incident beam on stagnation temperature and pressure has been reported by Palau et al.^[19]

When dealing with layered semimetal surfaces, the free electron gas is protected by an anion surface layer leading to an essentially hard-wall potential plus a more or less deep attractive van der Waals potential, k_{iz}^2 should be corrected due to the presence of the attractive well before being repelled by the hard wall (Beeby correction^[20]). This implies that both the incident and final normal momenta should be replaced by $k_z^2 \rightarrow k_z^2 + 2mD/\hbar^2$, where D is the attractive potential depth. Usually, the incident energy E_i is generally much larger than D , so that this correction can be neglected. With regard to

Equation (9), notice that the Beeby correction cancels out in the differential in the denominator, but retains a minor effect through the term in the numerator.

The high sensitivity of the HAS technique permits the detection of weak surface charge density waves (CDW) that are difficult to detect with other surface techniques. Recently, it has been shown that from the temperature dependence of the CDW diffraction peaks information about the e-ph interaction sustaining the CDW transition is possible.^[3] There is an instability below a critical temperature T_c generally induced by the e-ph coupling according to the theory developed by Fröhlich–Peierls^[21,22] or the Kelly–Falicov multivalley mechanism.^[23–25] In the latter case, the phonon-induced transitions between narrow pockets (nests) literally realize what is meant as perfect nesting. The occurrence of a CDW instability below T_c yields additional T -dependent diffraction peaks in the elastic scattering angular distribution at parallel wave vector transfers $\Delta\mathbf{K}$ equal or close to the nesting vectors $\mathbf{Q}_c$ (e.g., $\mathbf{Q}_c = 2\mathbf{k}_F$ for the 1D Peierls mechanism).

When examining the thermal attenuation for a given diffraction peak intensity due to the DW factor, the corresponding wave vector $\Delta\mathbf{K}$ transfer parallel to the surface equals to either a $\mathbf{G}$ -vector of the normal surface lattice ($\Delta\mathbf{K} = \mathbf{G}$), or to a CDW wave vector $\mathbf{Q}_c$. In this case, Equation (8) can also be applied to diffraction peaks by simply replacing $4k_{iz}^2$ by $\Delta k_z^2 + \Delta\mathbf{K}^2$. Usually in HAS experiments, the condition $\Delta\mathbf{K}^2 \ll \Delta k_z^2$ holds, therefore the T -dependence of the diffraction and specular peaks leads to a λ_{HAS} value which is independent of the diffraction channel. In Equation (1), the temperature dependence of $I(T)$ comes from thermal vibrations. However, this is no longer completely true when considering the diffraction from a surface CDW which forms below T_c from a Fermi surface instability. Clearly, the temperature-dependent population of electron states near the Fermi level follows Fermi statistics. Here, I_0 has an implicit dependence on T , which is generally negligible with respect to that of $W(T)$, except near T_c ; in this case, its square root $\sqrt{I_0}$ can be considered as an order parameter,^[26,27] and vanishes when $T \rightarrow T_c$ as $(1 - T/T_c)^\beta$, where β is the order-parameter critical exponent (typically $\beta = 1/3$).^[28–30] In the following, 1D electron gas (1DEG) examples are shown that, away from the critical region, a CDW diffraction peak may be used to extract λ_{HAS} .

The case of Bi(114), a topological surface exhibiting properties of a 1D free electron gas, as well as a CDW, has been discussed in an earlier letter.^[3] As shown in that letter, the weak 2D character of this surface, characterized by a long period (28.4 Å) in the $\overline{X}\overline{Y}$ direction, is responsible for the charge density wave, observed with HAS below $T_c \approx 280$ K, via the Kelly–Falicov multivalley $\overline{X} - \overline{X}$ nesting mechanism. The pronounced 1D metal character of Bi(114)^[31] is confirmed by the reliable value $\lambda_{\text{HAS}}^{(1D)} = 0.45$ obtained by treating it as a 1D system.

The H-saturated (110) surfaces of tungsten and molybdenum, despite the uniform distribution of the hydrogen atoms, which sit on hollow sites and form a lattice like that of the metal atoms, actually exhibit a pronounced 1DEG behavior along certain directions of the surface Brillouin zone (BZ) due to the favorable shape of surface state Fermi contours that provide good nesting conditions.^[32] Such a 1D character of the surface electron gas has become evident from the observation with HAS of a giant sharp Kohn anomaly in the Rayleigh wave dispersion

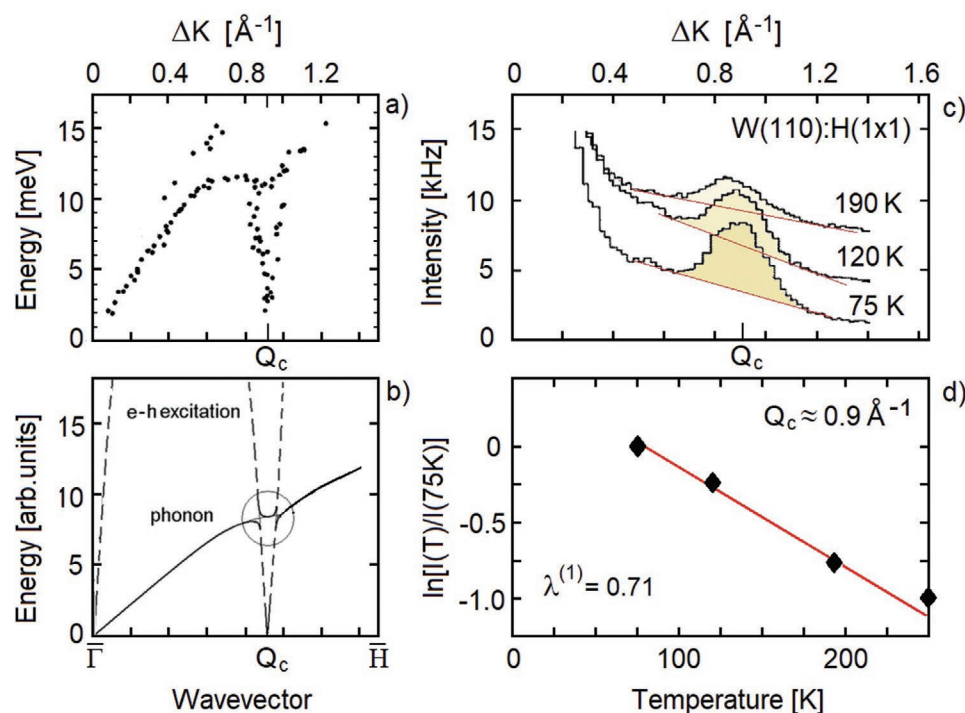


Figure 1. Helium atom scattering data from a hydrogen monolayer covering a tungsten (110) surface: W(110):H(1 × 1).^[29] a) The giant anomaly observed in the Rayleigh wave (RW) dispersion curve at $T = 130$ K^[33,34] originates from an avoided crossing [as depicted in (b)] with the electron–hole excitation spectrum of a 1DEG associated with the H(1 × 1) overlayer. Ab initio calculations by Kohler et al.^[32] indicate a Fermi-contour nesting vector $2k_F$ equal to the anomaly wave vector at Q_c . c) An HAS satellite diffraction peak at Q_c , suggesting the presence of a CDW, decreases with temperature with a linear dependence of the DW exponent as shown in (d). Deviations from linearity beyond $T \approx 250$ K are attributed to coexistence with a disordered phase^[36] and desorption around 400 K.^[33] The 1DEG e–ph coupling strength as derived from Equation (8) for dimensionality $d = 1$ is $\lambda_{HAS}^{(1D)} = 0.71$.

curve around the $\bar{\Gamma}\bar{H}$ and $\bar{\Gamma}\bar{S}$ directions, which are [001] and $[1\bar{1}2]$ in the direct space, respectively, in both W(110):H(1 × 1) [Figure 1a)] and Mo(110):H(1 × 1).^[33] As schematically represented in Figure 1b), the anomaly actually originates from the avoided crossing (encircled region) of the 1D electron–hole (e–h) excitation curve (broken line) with the phonon dispersion curve. As the increasing surface wave vector ΔK approaches the anomaly wave vector Q_c , the e–ph coupling gradually turns the phonon excitation (where atoms move and electrons follow adiabatically) into an e–h excitation (where the charge density oscillates while dragging the atoms less and less), and then reverts back to predominantly adiabatic phonon behavior as ΔK continues to increase beyond Q_c . Inside the small encircled region around Q_c , that is, in the vicinity of the anomalous behavior, the e–h excitation of the electron gas behaves like a phonon. Remember that He atoms are scattered by the surface charge density, and therefore exchange energy and momentum with the adiabatic phonons associated with the movements of the crystal cores, or with the anomalous (non-adiabatic) low-energy excitations of the surface nearly free-electron gas. The presence of an approximately 2 meV gap in the e–h branch at Q_c (although not much larger than the 1% energy resolution of the incident energy $E_i = 34.8$ meV) suggests critical fluctuations of an incipient CDW, consistently with the observation of a small satellite peak at $Q_c \approx 0.93 \text{ \AA}^{-1}$ in the HAS diffraction spectrum along $\bar{\Gamma}\bar{H}$ [Figure 1c)].^[34,35] The correspondence of the critical wave vector Q_c to a nesting on the Fermi contour lines at $Q_c = 2k_F$, as resulting from photo-emission data and

first-principle calculations, has been thoroughly discussed for both W(110):H(1 × 1) and Mo(110):H(1 × 1) by Kohler et al.^[32] The corresponding DW exponent decreases linearly with temperature [Figure 1d)], at least in the temperature region $T \leq 225$ K, beyond which the ordered H(1 × 1) phase starts coexisting with a disordered phase.^[36] The e–ph coupling constant λ_{HAS} for W(110):H(1 × 1) can now be extracted from the linear slope of the DW exponent. With the input data $\phi = 4.72$ eV for W(110):H(1 × 1),^[37] $r_0 = \pi/k_F = 6.98 \text{ \AA}$, and $(\Delta k_z)^2 + (2k_F)^2 = 108.9 \text{ \AA}^{-2}$ one obtains $\lambda_{HAS}^{(1D)} = 0.71$. This value compares well with the Rotenberg and Kevan result $\lambda = 0.8 \pm 0.2$, as derived from ARPES data collected along an azimuth close to the $\bar{\Gamma}\bar{H}$ direction (slice C in Figures 1 and 2 of their cited paper).^[38]

Unlike the CDW appearing in the case of Bi(114),^[3] where the 1D character of the surface electron gas is quite evident from the large separation of the surface atomic chains, in the case of W(110):H(1 × 1) the hydrogen atoms form a 2D lattice like that of the clean W(110) surface. Moreover, a similar symmetry is expected for the CDW from the calculated map of the local probability function for e–h excitations across the surface state Fermi contours.^[32] It is, therefore, plausible to derive $\lambda_{HAS}^{(2D)}$ from the same DW input data and compare it to $\lambda_{HAS}^{(1D)}$. From the ratio

$$\frac{\lambda_{HAS}^{(2D)}}{\lambda_{HAS}^{(1D)}} = \frac{\gamma_2}{\gamma_1} \frac{r_0}{k_F a_c} \quad (10)$$

where $\gamma_2/\gamma_1 = 2$ and $a_c = r_0^2/\sqrt{2}$ is the unit cell area for the CDW lattice. This gives $\lambda_{HAS}^{(2D)}/\lambda_{HAS}^{(1D)} = 2^{3/2}/\pi = 0.90$, which means that

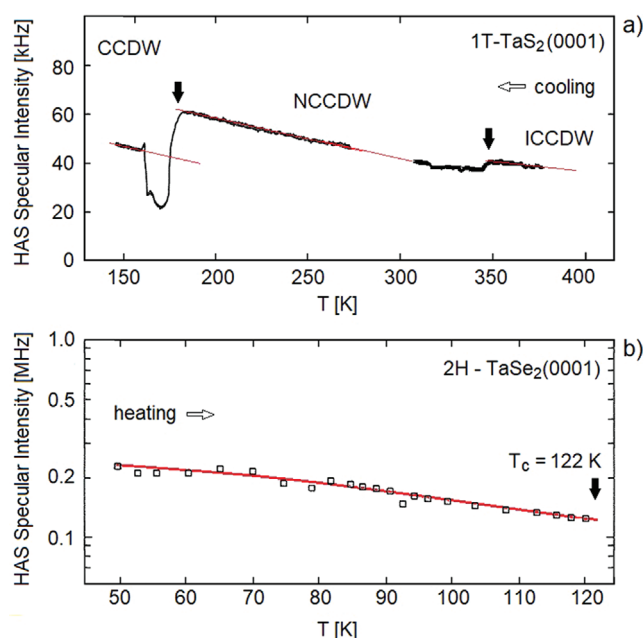


Figure 2. Thermal attenuation (Debye–Waller) data for scattering of He atoms from two chalcogenide surfaces. The specular intensity is plotted as a function of temperature. a) 1T-TaS₂(001) plotted on a linear scale, and b) 2H-TaSe₂(0001) plotted on a logarithmic scale. In (a), the crystal was initially at high temperature and then cooled, and the two vertical arrows indicate the charge density wave transitions. The transition from incommensurate charge density wave (ICCDW) to non-commensurate occurs at about 350 K, while the transition from non-commensurate to commensurate charge density wave (CCDW) occurs at about 180 K. In (b), the temperature was increased starting from the smallest T and the charge density wave transition occurs at 122 K as marked by the arrow. Data are from ref. [45].

also the 2D expression provides a reasonable approximation for $W(110):H(1 \times 1)$. Since Equations (8) and (9) have been derived for an isotropic nDEG, the deviation of the above ratio from

unity essentially measures the deviation from isotropy of the actual 2DEG.

The cases of recently measured topological Bi pnictogens Bi₂Se₃, Bi₂Te₃, and Bi₂Te₂Se have been considered elsewhere.^[3] In addition, several other chalcogenide crystal surfaces that have been investigated with He atom scattering are listed in Table 1. In all but one of these systems it was the specular thermal attenuation that was measured and two examples, for 1T-TaS₂ and 2H-TaSe₂, are shown in Figure 2.

Although the experiments on the chalcogenides did not involve layer-by-layer growth we can use for their analysis Equation (2) together with the definition of α of Equation (3) which leads to

$$\lambda_{HAS} = \frac{\pi}{2n_s} \alpha \quad (11)$$

with n_s given by

$$n_s = \frac{\pi \hbar^2 \mathcal{N}(E_F)}{m_e^* a_c} \quad (12)$$

The quantity n_s plays a role similar to n_{sat} in the case of layer-by-layer growth, that is, it is the number of layers whose electronic states at the Fermi level concur to give the surface charge density probed by the He atoms, and $\mathcal{N}(E_F)$ is their total density of states; thus $\mathcal{N}(E_F) = n_s a_c \mathcal{N}_F^{(2)}$. This implies that n_s represents the number of layers of the compound that are contributing to the value of λ_{HAS} as measured in a He atom collision with the surface. Equations (11) and (12) suggest that the question of determining the density of states $\mathcal{N}(E_F)$ appropriate to the reflection of atomic He is cast into the problem of determining a single parameter, namely the small number of layers n_s of the surface that contribute.

In semimetals and degenerate semiconductors, as well as in normal semiconductors with a degenerate accumulation layer at the surface, the density of states $\mathcal{N}(E_F)$ is associated with the presence of surface states and quantum-wells states

Table 1. The mass enhancement factor λ_{HAS} for some transition-metal chalcogenides as determined from the temperature dependence of the thermal attenuation of elastic specular He atom diffraction. When not explicitly specified in the text, the uncertainty in the derived values of λ_{HAS} is estimated to be of the order of 10 % or less. Besides the known experimental error in the DW exponent slopes, it includes the uncertainties in the parameters entering Equation (9), not always given in literature. The entry for PtTe₂ was evaluated from the dependence on incident angle of the diffuse elastic peak intensity at a constant temperature of 100 K. The two different values of λ_{TF} and λ_{HAS} reported for MoS₂ correspond to two samples with surface carrier concentrations of 5 and $7 \times 10^{12} \text{ cm}^{-2}$, respectively.^[39] The Beeby correction D for MoS₂ is 13.6 meV.

Surface	T range [K]	$k_i^2 [\text{\AA}^{-2}]$	ϕ [eV]	$\lambda_{TF} [\text{\AA}]$	λ_{HAS}	λ (other sources)
2H-MoS ₂ (001) ^[39]	95–450	121	5.2 ^[40]	9.8 ^[41]	0.41	≈ 0.1 ^[42,43]
				9.3	0.49	0.12–0.20 ^[44]
1T-TaS ₂ (001) ^[45]	180–280 ^[46,47] 350–380 ^[51]	29.2	5.2 ^[48]	10.2 ^[49]	1.0 ^[47] ~ 0.4 ^[51]	1.0 ^[50] 0.69–2.09 ^[28] 0.38 ^[52]
2H-TaSe ₂ ^[45]	50–120	137	5.5 ^[53]	12.6 ^[54]	0.58	0.49 ^[50] 0.39 ^[55]
1T-PdTe ₂ (001) ^[56]	50–300	121	4.6 ^[57]	10.62 ^[56]	0.58	0.59 ^[58] 0.53 ^[59]
1T-PtTe ₂ ^[60]	100	159	4.52 ^[57]	10.4 ^[60]	0.40 ± 0.02	0.35 ^[59]

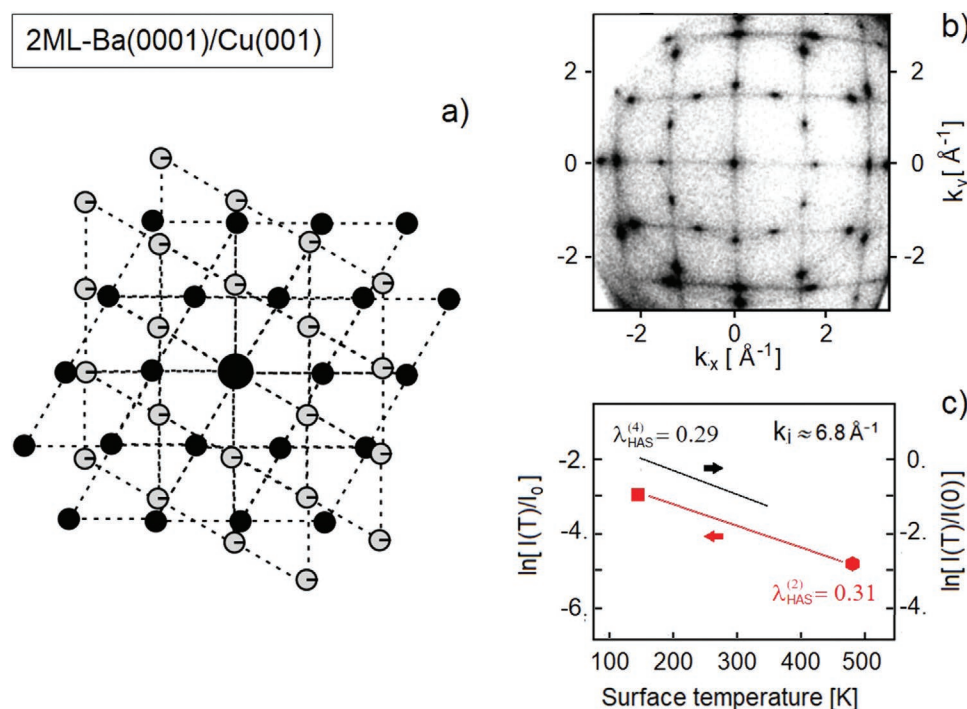


Figure 3. The surface of two monolayers of Ba(0001) on Cu(001). a) A Ba bilayer grown on Cu(001) at growth stage III^[66] exhibits a dodecagonal QC structure corresponding to the LEED pattern shown in b) The structure is a superposition of two hexagonal 2D lattices with a 30° twist, and is the projection of a 4D {3, 3, 4, 3} honeycomb lattice.^[65] c) The HAS reflectivity DW exponent measured at two different temperatures and the same incident wavevector $k_i = 6.8 \text{ \AA}^{-1}$ allows derivation of the e–ph coupling constant by either treating the bilayer as a 2D ($\lambda_{\text{HAS}}^{(2D)}$) or a 4D ($\lambda_{\text{HAS}}^{(4D)}$) system, with little difference between the two results. The latter is closer to the current value for bulk barium ($\lambda = 0.27$) as reported by Allen.^[6]

confined within the band bending, that is, within the Thomas–Fermi (TF) screening length λ_{TF} .^[61] In transition-metal layered compounds the limited electron mobility in the normal direction, resulting in a large effective mass anisotropy, makes λ_{TF} comparatively short, typically spanning about two triple layers. Thus $n_s \approx 2$ appears to be an appropriate value for this class of materials (see Table 1). Pnictogen chalcogenides, whose e–ph coupling strength as derived from HAS measurements have been presented and discussed elsewhere,^[3] are characterized by screening lengths an order of magnitude larger than in transition metal chalcogenides, due to their quintuple layer structure with a more pronounced 3D character. As a consequence, their λ_{HAS} is seen to receive a far larger contribution from the surface quantum-well states than from the topological Dirac states.

Table 1 lists some chalcogenides, not including the Bi pnictogens considered in ref. [3], for which sufficient temperature-dependent data are available for He atom scattering, together with the corresponding references, the relevant experimental parameters, and the values obtained for λ_{TF} . In each case shown in Table 1, with reasonable choices for λ_{TF} determined using parameters taken from the literature, results for λ_{HAS} are in fairly good agreement with values of λ determined from other known sources, which may be either bulk measurements or calculations. The entry for PtTe₂ differs from the others in that the elastic peak measured was not the specular one but the off-specular diffuse elastic peak measured at the constant temperature of 100 K. In this case, the incident angle was varied, keeping the source-to-detector angle fixed. Thus, Equation (3)

was modified to account for the correct wave vector difference, that is, $k_{\text{iz}}^2 \rightarrow \Delta k^2/4 = (\mathbf{k}_f - \mathbf{k}_i)^2/4$, and the factor α changes to reflect the fact that the intensities were evaluated at different incident angles, but at constant T .

Quasi-crystals (QC) are characterized by a long-range orientational order^[62–64] but no periodicity. They can be viewed as projections onto the ordinary space of a periodic lattice in a space nD of higher dimension.^[65] Certain structural and dynamical properties of the QC may be more conveniently described in the corresponding nD periodic lattice. This representation is adopted here to derive the e–ph coupling constant for two QC metallic structures, a dodecagonal bilayer and a 3D decagonal QC, respectively, represented by periodic 4D and 5D lattices.

The LEED pattern for a barium bilayer grown on Cu(001) at the growth stage denoted as III by Bortholmei et al.^[66] exhibits a dodecagonal QC structure as shown in Figure 3a,b. The structure is a superposition of two hexagonal 2D lattices with a 30° twist. A twist of any angle other than integer multiples of $\pi/3$ breaks the hexagonal periodicity of a single layer while keeping a long-range orientational order. The present structure can be generated by the projection of a 4D {3, 3, 4, 3} honeycomb lattice (actually a 4D body-centered-cubic (bcc) lattice).^[65]

The DW exponent measured from the HAS reflectivity $I(T)$ as a function of temperature at a given incident wave vector $k_i \approx 6.8 \text{ \AA}^{-1}$ as shown in Figure 3c,^[66] allows the derivation the e–ph coupling constant from Equation (8) for dimensionality $d = 4$ using two different estimates. First, the temperature dependence of $2W(T)$ has been obtained using the Debye temperature $\Theta_D = 120 \text{ K}$ reported in Ref. [66] for the stage III Ba bilayer in

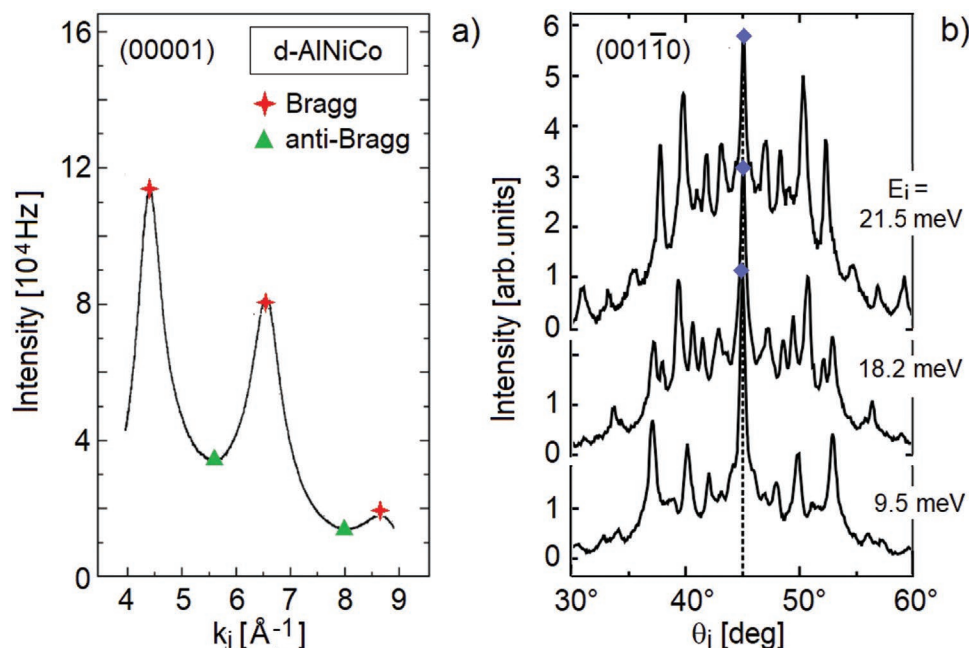


Figure 4. a) HAS reflectivity of the d-AlNiCo(00001) surface measured by Sharma et al.^[71] as function of the incident wave vector at room temperature, with the scattering plane along the symmetry direction [10000]. The large oscillations are due to constructive interference (Bragg, marked with red stars) or destructive (anti-Bragg, marked with green triangles) interference at surface steps. b) HAS diffraction patterns from the d-AlNiCo (001 $\bar{1}$ 0) surface measured at different incident energies and room temperature along the [10000] direction. The specular peak (blue diamonds) intensities are derived after subtraction of the multiphonon Gaussian background. The incident energies fulfill approximately Bragg conditions (adapted from Sharma et al.^[73]).

the temperature range 150–350 K using the prescription of ref. [67], where M is the Ba atom mass. This gives a slope of 77.2 eV^{-1} [Figure 3c, black line]. A second method is the direct derivation of the slope from reflectivity at two different temperatures, 480 and 145 K, which gives a similar value of 67.9 eV^{-1} [Figure 3c, red line connecting the two data points], although the low-temperature bilayer structure shows a pronounced fourfold symmetry, compatible with the 2D periodicity of the bcc-Ba(001) surface.^[66] With the slope of 77.2 eV^{-1} , $\gamma_4 = 8\pi^2$, taking as a simple estimate $\phi = 2.7 \text{ eV}$ ^[68] and $k_F = 0.28 \text{ Å}^{-1}$ for Ba metal,^[69] and r_0 (where r_0^4 gives the 4D-bcc hypercell volume) equal to the lattice parameter of bcc Ba (5.03 Å), it is found that $\lambda_{HAS}^{(4D)} = 0.29$. For comparison, the slope of 67.9 eV^{-1} used with the 2D version of Equation (9) gives $\lambda_{HAS}^{(2D)} = 0.31$. The value of $\lambda_{HAS}^{(4D)}$ is closer to the current value for bulk barium ($\lambda = 0.27$) as reported in ref. [6], but the difference is not particularly significant at the present level of approximation.

The surface structure and dynamics of the decagonal quasicrystal $\text{Al}_{71.8}\text{Ni}_{14.8}\text{Co}_{13.4}$ (approximately Al_5NiCo), hereafter termed d-AlNiCo, have been investigated by HAS for the surfaces (00001)^[70–72] and (001 $\bar{1}$ 0)^[73] of the nominal 5D generating periodic lattice.^[65] The available data permit determination of information on the dependence of the specular intensity on the incident momentum and hence evaluation of the e-ph coupling constant by using Equation (9).

Figure 4a) shows the HAS specular intensity for the (00001) surface of d-AlNiCo reported by Sharma et al.^[71] as a function of the incident wavevector in a 90° scattering geometry ($k_{iz} = k_i/\sqrt{2}$) at room temperature. The large oscillations are due to the interference between beams reflected above and below

a step: the maxima (Bragg scattering) occur when $k_{iz} = \pi n/s$, with s the step height and n an integer; the minima (anti-Bragg scattering) where $k_{iz} = \pi(n + 1/2)/s$ (here $n = 2, 3, 4$). The step height corresponding to the peak positions $s = 2.06 \text{ Å}$ ^[71] is that of a monolayer, in agreement with the bilayer periodicity of $\sim 4 \text{ Å}$ reported by Rogalev et al.^[74] The average slopes of the Bragg and anti-Bragg peak intensities as functions of k_{iz} are $-\partial \ln(I/k_i)/\partial(k_{iz}^2) = 0.086 \pm 0.017 \text{ Å}^{-2}$ (Bragg) and 0.056 Å^{-2} (anti-Bragg). The difference between the two slopes indicates an appreciable contribution of the steps to the e-ph coupling, which is present in Bragg scattering and less so in anti-Bragg scattering. The HAS diffraction patterns have also been measured by Sharma et al.^[73] for the d-AlNiCo surface at three different incident energies along the quasi-periodic [10000] direction as shown in Figure 4b). The dependence on the incident wavevector of the specular elastic peak intensity, after subtraction of the multiphonon bell-shaped background, is given by $-\partial \ln(I/k_i)/\partial(k_{iz}^2) = 0.080 \pm 0.021 \text{ Å}^{-2}$.

Soft X-ray angle-resolved photoemission spectroscopy (SX-ARPES) data by Rogalev et al.^[74] from d-AlNiCo(00001) provide information on the projection of the 5D Fermi surface onto various cuts of the 3D reciprocal space like the one, reproduced in Figure 5c, taken parallel to the (x, y) plane at $k_z = 9(2\pi/c)$ where $c = 4 \text{ Å}$ is the surface bilayer thickness, periodically repeated in the z direction [00001]. As it appears from this cut of SX-ARPES data, $k_F = 0.9 \text{ Å}^{-1}$ seems to be a reasonable choice (Figure 5c). Then, with $\phi = 4.8 \text{ eV}$ from $\text{He}^*(2^3S, 1s2s)$ de-excitation spectroscopy,^[75] $r_0 \cong 6.0 \text{ Å}$ from the value of the reciprocal quasi-lattice vector $G = 1.04 \text{ Å}^{-1}$ derived from the HAS dispersion curves in the [10000] direction^[70]

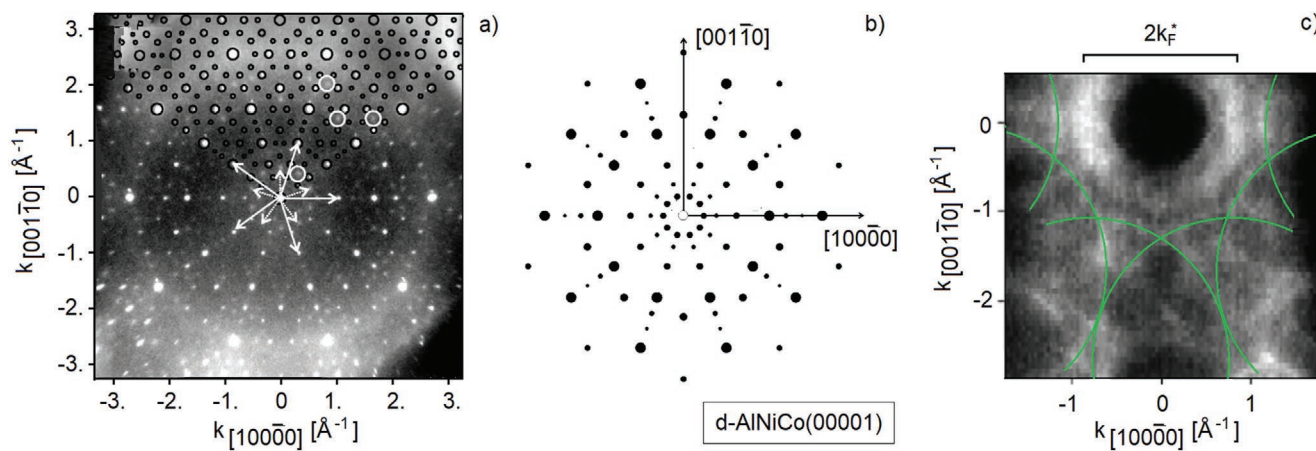


Figure 5. a) Spot profile analysis low-energy electron diffraction (SPA-LEED) image of d-AlNiCo(00001), with indication of the basis vectors (arrows) of b) the 5D reciprocal lattice (reproduced from ref. [71]), and c) a Fermi surface cut as imaged by SX-ARPES along a plane parallel to the surface at $9G_z$ ($G_z = 2\pi/c$) (adapted from Ref. [74]) with the indication at the top of panel c) of the diameter $2k_F = 1.8 \text{ \AA}^{-1}$ of the most prominent Fermi contour. The green circles represent the Al *sp*-band Fermi contours of diameter $2k_F^0 = 3.14 \text{ \AA}^{-1}$.^[74]

(but also from reflection high-energy electron diffraction (RHEED) data^[75]) and $k_B T = 0.026 \text{ eV}$, Equation (9) gives $\lambda_{HAS}^{(5D)} = 0.26 \pm 0.05$ (Bragg) and 0.17 (anti-Bragg) for the d-AlNiCo(00001) surface. As argued above, the larger value of $\lambda_{HAS}^{(5D)}$ obtained from Bragg reflectivity may be attributed to an enhancement of the e-ph interaction at steps. With the HAS data for the (001 $\bar{1}0$) surface and the same input parameters k_F , ϕ , r_0 , and $k_B T$ given above one finds $\lambda_{HAS}^{(5D)} = 0.24 \pm 0.06$. The similarity of this value with that for the (00001) surface including steps can be understood from the fact that the (001 $\bar{1}0$) surface actually exhibits (00001) facets,^[73] which can a posteriori justify the use of the same (00001) input data for the derivation of $\lambda_{HAS}^{(5D)}$.

Finally, it is interesting to discuss the possibility that the e-ph interaction probed by HAS is actually restricted to the surface, so that Equation (9) with dimension $d = 4$ is more appropriate. In this case the same input data yields slightly larger values for the e-ph coupling, $\lambda_{HAS}^{(4D)} = 0.29 \pm 0.06$ (Bragg) and 0.20 (anti-Bragg) for the d-AlNiCo(00001) surface, and 0.22 ± 0.06 for the (001 $\bar{1}0$). Considering that also the HAS reflectivity data for the (001 $\bar{1}0$) surface are approximately under Bragg conditions, the comparison with the Bragg value of $\lambda_{HAS}^{(4D)}$ for the (00001) surface indicates an appreciable anisotropy, which favors the quasicrystalline plane. These values can be compared with the mass-enhancement factor extracted from the e-ph enhancement of thermoelectric power (TP) measurements in Y-AlNiCo, the monoclinic 3D approximant of decagonal d-AlNiCo.^[76] At room temperature the fit in the a^* direction (approximating [10000] in the decagonal sample) gives $\lambda_{TP} \sim 0.2$, a value which appears, however, to increase at lower temperature.^[76] There is significant anisotropy, with λ_{TP} for the quasicrystalline plane about five times larger than along the tenfold axis. Moreover, λ_{TP} exhibits a large increase for decreasing T , though the present value $\lambda_{HAS}^{(4D)} = 0.28$ from room temperature HAS data would correspond to the Shuyuan et al. TP data at about 130 K.^[77]

It may be argued that an ideal free-electron model does not contain information on the lattice periodicity or quasicrystallinity. With this in mind, the 5D d-AlNiCo can also be treated as a 3D system with a Fermi surface from the highly-

dispersed Al *sp*-band ($k_F^0 = 1.57 \text{ \AA}^{-1}$).^[74] In this case, with the same ϕ and r_0 , one finds $\lambda_{HAS}^{(3D)} = 0.23 \pm 0.05$ (Bragg) and 0.15 (anti-Bragg) for the d-AlNiCo(00001) surface, and 0.22 ± 0.06 for the (001 $\bar{1}0$). It appears that, within the experimental uncertainties, the effects of dimensionality are in this case rather modest. On the other hand, it is easily seen that treating d-AlNiCo(00001) as a 2D system, with the response restricted to the surface bilayer ($n_{\text{sat}} = 2$), the ratio $\lambda_{HAS}^{(2D)} / \lambda_{HAS}^{(4D)} = (r_0 k_F)^2 / 4\pi n_{\text{sat}}$ is for this case equal to 1.16. Thus, in this case, like for 2ML-Ba/Cu(001), the 2D treatment yields only a slightly larger e-ph coupling constant than that obtained from the treatment with the more appropriate dimensions.

Herein, we have analyzed the thermal dependence of the Debye–Waller factor measured in the scattering of atoms from a selection of complex surface systems in order to extract values of the electron–phonon coupling constant λ . The analysis is based on a theory originally developed for obtaining λ for metal surfaces, but which here is adapted to the more complicated cases of layered chalcogenide semiconductors and systems that can be considered as having different dimensions such as 1D CDWs and quasicrystals. The original theory demonstrates that the argument of the Debye–Waller factor $2W(k_F, k_i, T)$ is, to a good approximation, proportional to λ . The current analysis shows that, with suitable interpretation of the theory, values of λ can be obtained from the surfaces of these more complex systems. For all of these systems, the values of λ_{HAS} obtained from atom-surface scattering experiments compare favorably with established values for the bulk materials as published in the literature. The uncertainty in the slopes of the Debye–Waller plot is not the only uncertainty in our calculations, because uncertainties in other parameters extracted from the literature are not always given. We estimate that the overall uncertainty in λ_{HAS} is 10 % or less.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electron–phonon interaction, helium atom scattering, high-dimensional materials, quasi-one-dimensional metals, transition metal chalcogenides

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