

Temperature dependence of resonance signatures in atom-surface scattering

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We present experimental data for the elastic resonant scattering of a thermal-energy He beam by a vicinal Cu surface over a large range of surface temperatures. We develop the theory for inelastic effects under resonant conditions and obtain excellent agreement for the increase in resonance linewidth with temperature. We conclude that the dominant perturber of the line shape at low temperatures is surface disorder.

I. INTRODUCTION

After Stern and co-workers demonstrated diffraction of thermal energy helium beams by solid surfaces,¹ one of the first discoveries was a series of resonances which were called selective adsorption.² These resonances, which appeared as narrow minima in the diffracted intensities, were correctly interpreted as being due to elastic diffraction into the bound states of the surface adsorption potential well.³ It was assumed that they always appeared as minima because, while passing through the diffraction channel in the well, the particle has a large probability amplitude near the surface and would be strongly scattered by inelastic processes involving phonons.

More recent experiments using monoenergetic beams and well-characterized surfaces have demonstrated a rich variety of resonant features (in the diffracted-beam intensities) whose signatures include dips, peaks, and mixed structures.^{4,5} For the case of He scattering from LiF surfaces, good agreement between experiment and theory has been obtained using purely elastic potentials^{6,7} with no need for additional inelastic scattering. In fact, very straightforward schemes have been developed for determining the signature of a particular resonance.^{8,9} For many other systems, however, a purely elastic calculation is insufficient to give the correct signatures or linewidths. Particularly in the case of vicinal metal surfaces, where strong resonant scattering is observed,¹⁰ the relatively weak corrugations produce calculated elastic resonance widths which are far too narrow and signatures which are often completely wrong.¹¹ In many instances good agreement has again been obtained by mimicking inelastic losses through the use of imaginary terms in the potential^{12,13} or by introducing effective Debye-Waller factors at intermediate points in the scattering process,^{11,14} although these approaches have not always been completely successful.¹⁵

Relatively few experimental studies exist on the surface-temperature dependence of resonances.^{16,17} This is probably because most studies of resonances have been

done either on lithium fluoride and other alkali-metal halides or on graphite, and the range of temperatures experimentally available was less than the relatively large Debye temperatures. On the other hand, metal surfaces provide a class of materials for which experiments can be readily performed over a range of temperatures extending both below and above the Debye temperature. In this paper we report measurements of the linewidths of resonances for the system of He scattering from a Cu(115) vicinal surface as a function of temperature. We also systematically develop a theory for treating inelastic effects in the presence of resonances. When the theory and experiment are compared for the He/Cu(115) system, we find that the temperature-dependent enlargement of the resonance widths is correctly predicted, but the actual widths are not. Based on this, and evidence from other experiments on vicinal metal surfaces, we conclude that the width and signature of such resonances at low temperature are strongly affected by disorder on the surface and much less so by inelastic effects. In particular, multiphonon-scattering events do not contribute strongly under resonance conditions at lower temperatures.

II. THEORY

We develop the theory within the framework of the distorted-wave or two-potential formalism. The total interaction potential V between particle and surface is divided into two parts $V=U+v$, where U is a static, surface-averaged contribution and v contains all diffraction and inelastic effects. (An alternative approach is to let U be the thermal average of V , i.e., $U=\langle V \rangle$, in which case it will already describe elastic diffraction.^{18,19}) Then the transition operator obeys the equation

$$T = v + vGT \quad (1)$$

We examine the elastic resonances by projecting them out.^{6,11,20} We write the total projection operator P for the distorted Hamiltonian as $P=P_1+P_b$, where P_b is the projection operator for a small subset of bound states in the neighborhood of resonance conditions. A straightfor-

ward manipulation converts Eq. (1) into two coupled equations,

$$T = \tau + \tau P_b G P_b T, \quad (2)$$

$$\tau = v + v P_1 G P_1 \tau. \quad (3)$$

Assuming τ to be known, the T operator (2) involves only the small subset of bound states. We rewrite it as

$$T = \tau + \tau P_b G_\tau P_b \tau, \quad (4)$$

where G_τ obeys the Dyson-type equation

$$G_\tau = G + G P_b \tau P_b G_\tau. \quad (5)$$

Equation (5) is the starting point of our treatment, but first we need to discuss the evaluation of τ which is itself the transition operator for a system with the small subset of bound states projected out. Equation (3) for the operator τ is of the form of a transition-operator equation, but the projection of the bound states makes τ correspond to the transition operator for a nonlocal potential.¹¹ We divide the potential v into an elastic part $v^0 = \langle v \rangle$ and an inelastic part v' ,

$$v = v^0 + v'. \quad (6)$$

Then another standard manipulation of Eq. (3) for τ leads to the coupled set

$$\tau = l + h + h P_1 G P_1 \tau, \quad (7)$$

with

$$l = v^0 + v^0 P_1 G P_1 l, \quad (8)$$

$$h = v' + v^0 P_1 G P_1 h. \quad (9)$$

An important observation from Eq. (7) is that τ can be divided into a purely elastic part l and a remainder $R = h + h P_1 G P_1 \tau$ which involves the inelastic part of the potential v' .

To evaluate scattering intensities, one needs, in general, the thermal average of the squared T matrix, $\langle T^2 \rangle$. However, for obtaining elastic diffraction peak intensities²¹ this is equivalent to $\langle T \rangle^2$. Thus we can obtain the resonance linewidths by directly averaging Eq. (4). For example, we can, to lowest order, neglect all inelastic interactions by setting $v' = 0$, which leaves $\tau = l$, and specializing to the case where P_b projects out only a single isolated resonant state labeled by the set of quantum numbers b , we have, for the transition amplitude to the final diffraction state f ,

$$\langle T_{fi} \rangle = l_{fi} + \frac{l_{fb} l_{bi}}{E_i - E_b - l_{bb}}. \quad (10)$$

This is the well-known amplitude for an isolated elastic resonance.^{11,20} The resonance linewidth is given by $\Gamma = 2 \text{Im} l_{bb}$ and the energy shift by $\text{Re} l_{bb}$.

Averaging Eq. (4) for T directly is an intractable problem, but we can develop it using Eq. (5) as an iterated series in orders of τ as follows:

$$T = \tau + \tau P_b G P_b \tau + \tau P_b G P_b \tau P_b G P_b \tau + \dots \quad (11)$$

We can then, in principle, average each term individually. If we carry out this averaging process for a sufficient number of terms to get the lowest corrections to the lifetime Γ , the result can be resummed, giving the following form, to first order;

$$\langle T_{fi} \rangle = \langle \tau_{fi} \rangle + \frac{\langle \tau_{fb} \rangle \langle \tau_{bi} \rangle}{E_i - E_b - l_{bb} - \langle R_{bb} \rangle - \langle R P_b G P_b R \rangle - \langle R \rangle P_b G P_b \langle R \rangle}, \quad (12)$$

where $G_l^{-1} = G^{-1} - l$. Equation (12) reduces to (10) if there is no inelastic scattering. This is clear since from the discussion after Eq. (9) we have $\tau = l + R$ and, in the absence of inelastic scattering, $R = 0$. Thus the first inelastic correction to the resonance width is $\Delta\Gamma = \text{Im} \langle R_{bb} \rangle$, and the other R -dependent terms in the denominator of the resonant term of (12) are higher-order inelastic corrections.

Equation (12) also shows that there is a substantial difference in the thermal attenuation (or Debye-Waller effect) of a diffraction peak, depending on whether it is or is not under resonance conditions. Off resonance, the second term on the left-hand side of (12) is negligible; the diffraction intensity is then proportional to $|\langle \tau_{fi} \rangle|^2$ and this is the starting point that has been used for the development of a successful theory of thermal attenuation.²² Under resonant conditions, the second term on the left-hand side of Eq. (12) dominates and the thermal attenua-

tion of the resonance height is governed by $|\langle \tau_{fb} \rangle \langle \tau_{bi} \rangle|^2$, the square of the product of two thermally arranged matrices. This behavior is evident in the experimental data of Fig. 1, where the height of the resonance peak is attenuated with temperatures much more strongly than the off-resonant intensity in the wings to either side. We can proceed to evaluate $\text{Im} \langle R_{bb} \rangle$ using an approach which has been very successful in explaining the thermal attenuation of diffraction peaks from smooth Cu surfaces.²² It is a good approximation to take the inelastic potential v' to be linear in the phonon variables; then the first nonvanishing contribution is $\langle R \rangle = \langle h P_1 G P_1 h \rangle$ and, upon approximating h by v' , we have

$$\langle R_{bb} \rangle \approx \sum_{l \neq b} \langle v'_{bl} G v'_{lb} \rangle. \quad (13)$$

The thermal average can be carried out upon using the integral representation for the Green function,

$$G = \frac{1}{E_i - H_0 - U + i\epsilon} = \frac{-i}{\hbar} \int_0^\infty dt e^{i(E_i - H_0 - U + i\epsilon)t/\hbar}, \quad (14)$$

and transforming the potentials into time-dependent operators in the interaction picture.²² If the off-

resonance diffraction intensities are small, we are justified in neglecting the sum over reciprocal-lattice vectors appearing in Eq. (13), which is equivalent to taking the inelastic part of the scattering as due to a surface which is flat in the absence of vibrations. The details of the averaging procedure have been presented elsewhere²² and the result is

$$\langle R_{bb} \rangle = \frac{1}{2\pi} \int_0^\infty dp \int \frac{d\omega}{\omega} \frac{|v'_{bp}|^2 \rho(\omega) n(\omega)}{[p_i^2 + K_i^2 - p^2 - (\mathbf{K}_i + \mathbf{B})^2] \hbar^2 / 2m + \hbar\omega + i\epsilon} + \sum_{m \neq b} \int \frac{d\omega}{\omega} \frac{|v'_{bm}|^2 \rho(\omega) n(\omega)}{[p_i^2 + K_i^2 - (\mathbf{K}_i + \mathbf{B})^2] \hbar^2 / 2m + |\epsilon_m| + \hbar\omega + i\epsilon}, \quad (15)$$

where p_i and \mathbf{K}_i are the incident normal and parallel wave vectors, respectively, \mathbf{B} is the reciprocal-lattice vector coupling to the resonant bound state, $\rho(\omega)$ is the phonon spectral density, and $n(\omega)$ is the Bose-Einstein factor. The imaginary part comes from the energy denominator pole, giving

$$\Delta\Gamma = 2 \operatorname{Im} \langle R_{bb} \rangle = -\frac{1}{2} \int_{|\epsilon_b|/\hbar}^\infty \frac{d\omega}{\omega} \rho(\omega) n(\omega) \frac{|v'_{bq}|^2}{q} + 2\pi \sum_{m \neq b} \frac{|v'_{bm}|^2 \rho(\omega_m) n(\omega_m)}{\hbar\omega_m}, \quad (16)$$

where $q = \hbar(\hbar\omega - |\epsilon_b|)^{1/2} / \sqrt{2m}$ and $\hbar\omega_m = |\epsilon_b| - |\epsilon_m|$, with $|\epsilon_b| = \hbar^2[p_i^2 + K_i^2 - (\mathbf{K}_i + \mathbf{B})^2] / 2m$, and ϵ_m is the energy of the bound state. For the numerical results presented below, we have evaluated Eq. (16) using the spectral density $\rho(\omega)$ for a Cu surface, and the matrix elements v'_{bp} are taken for $v' = D e^{-2\kappa z}$ (the repulsive part of the He-Cu potential) and Morse-potential eigenstates. This potential, with $D = 6.35$ meV and $\kappa = 1.05 \text{ \AA}^{-1}$, has given good agreement with experiment for a wide range of elastic- and inelastic-scattering data.^{22,23} There are, consequently, no adjustable parameters.

III. EXPERIMENT

Several sets of experimental data are shown in Fig. 1 for a 21-meV He beam incident on a vicinal Cu(115) surface where the resonance with the lowest, $n=0$ ($|\epsilon_b| = 4.58$ meV), bound state occurs at the incident angle $\theta_i \approx 72^\circ$. The measured specular peak height is plotted as a function of incident angle, giving the resonance shape. Note that as θ_i is varied the angular position θ_f of the diffraction peak also varies. The data, taken at a wide range of surface temperatures, show that not only is the resonant intensity attenuated with increasing temperature, but it also is broadened. The full width at half maximum (FWHM) for both the specular (00) peak and the (10) diffraction peak are shown in Fig. 2. [The resonance appears as a minimum for the $(\bar{1}0)$ intensity.] The FWHM for both resonances has a low-temperature value of approximately 1.4° and then rises linearly with temperature until it reaches the neighborhood of 400 K, where it increases rapidly with temperature. It has been shown²⁴ that for the (115) face this temperature corresponds to the boundary of two regimes. Above this temperature

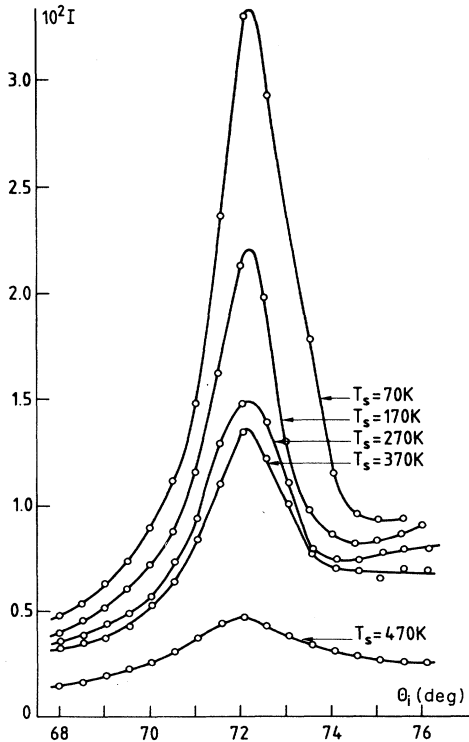


FIG. 1. The specular (00) intensity of 21-meV He incident on a Cu(115) surface near resonance with the $n=0$ (ground state) bound level, for several surface temperatures. The incident beam is directed at the angle θ_i into the step faces.

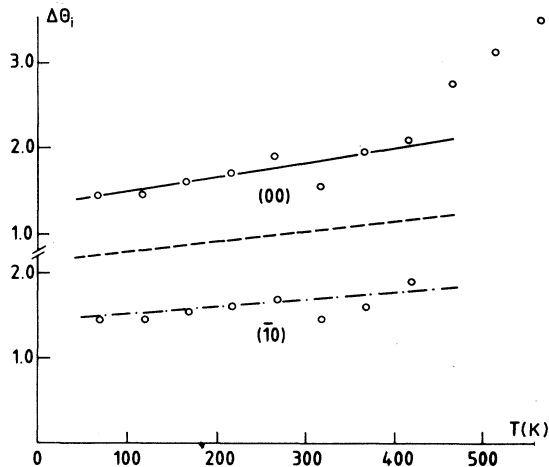


FIG. 2. The full width at half maximum $\Delta\theta_i$ of the $n=0$ resonance as a function of surface temperature as seen in the (00) specular and (10) diffracted intensities, for the same conditions as in Fig. 1. The solid lines are least-squares fits to the data points for $T \leq 420$ K, and for reference the dashed line gives the theoretically calculated slope.

the number of defects gathered in domains increases due to the onset of thermal roughening.²⁴ Below this temperature substantial disorder of this type remains because the relaxation times of defects are so long that the defects are effectively frozen in.²⁵ This domain structure gives rise to phase-antiphase oscillations which can be observed in the intensity of diffraction peaks.^{26,27} For the present experiment, phase and antiphase conditions are widely separated in angles, occurring at $\theta_i = 45^\circ$ and 69.3° , respectively. Hence the temperature dependence of the resonance shape will be essentially unaffected by the slight variation of phase occurring in the small region of $\theta_i \cong \pm 2^\circ$ around the resonance maximum. It has been shown that the peak shape under antiphase conditions does not broaden appreciably in the temperature range 70–400 K,²⁷ this indicates that the number of surface defects does not vary substantially. One does not expect the number of defects to change appreciably over this temperature range since they are governed by an activation-type process. This small broadening of the diffraction peak with temperature will have a negligible effect on the measurement of the resonance width, since the latter is obtained by varying θ_i over several degrees. No shift of the resonance maximum with temperature is detected. The measured resonance width is then governed primarily by the exchange of real and virtual phonons, which corresponds to the theoretical calculations discussed above. The slope of the linear part of the experimental curves shown in Fig. 2, as determined by a least-squares fit of the points through $T = 420$ K, is $d\theta/dT \cong 0.0017$ deg/K for the (00) beam and $\cong 0.0009$ deg/K for the (10) beam. Rather striking agreement is obtained when the above experimental results are compared with calculations from Eq. (16). First we find that $\Delta\Gamma$ is linear in T for temperatures above 70 K, which arises directly from the $kT/\hbar\omega$ behavior of $n(\omega)$ at large T . For small Γ ,

$\Delta\theta_i$ is proportional to $\Delta\Gamma$ and we obtain $d\theta_i/dT = 0.0012$ deg/K for the $n=0$ resonance, which is surprisingly close to the experimental values in view of the first-order nature of the theory. Additionally, we find that $d\theta_i/dT = 0.0013$ for the $n=1$ resonance, and 0.0008 for $n=2$. The higher-order corrections to $\Delta\Gamma$ appearing in the denominator of Eq. (12) were evaluated with a slightly cruder model and their contribution was found to be negligible, as they are more than an order of magnitude smaller than Eq. (16). The real part of $\Delta\Gamma$ has been estimated from Eq. (15) and, although it is also linear in temperature for $T > 70^\circ$, it is negligible in comparison with the incident energy, indicating no detectable shift of the resonance angle, in agreement with experiment.

The success of a first nonvanishing-order theory in explaining all of the above experimental features is a strong indication that there is no unusually large inelastic interaction with the He atoms under conditions of resonance. The linear behavior in T indicates that single-phonon processes are dominant, as multiphonon events contribute as higher powers of T . The thermal attenuation (or Debye-Waller damping) is substantially stronger at resonance than off resonance as is clearly seen in Fig. 1. However, this is predicted by our theory, since as discussed above the resonant term in Eq. (12) contains two thermally averaged transition matrices in the numerator, while off resonance only the single term $\langle \tau_{fi} \rangle$ contributes.

We now come to the question of the FWHM at low temperatures, which is given by $\Gamma = 2 \text{Im}l_{bb}$ in Eqs. (10) or (12), since the temperature-dependent corrections are negligible there. Calculations of l_{bb} using potentials that are known to provide excellent fits to the nonresonant diffraction intensities give a Γ which is too small to predict the observed $\Delta\theta_i$. For example, Figs. 1 and 2 show that at low temperatures $\Delta\theta_i = 1.4^\circ$, while the corresponding calculations predict $\Delta\theta_i = 1.04^\circ$. A more extreme case occurs for He/Cu(113), where the calculations produce resonance widths of about 0.1° and even predict the wrong signature, while the experiment gives approximately 0.6° .¹¹ Thus there must be some other mechanism in play and the most likely candidate is scattering from frozen-in disorder on the surface as explained above. Such an interpretation is consistent with previous calculations using optical-type potentials^{12,13} to obtain agreement with the experimental resonance widths. For such crude models, the loss of unitarity or decrease in intensity caused by an imaginary term in the potential cannot distinguish as to whether this loss is due to static disorder or inelastic effects. Assuming that the additional linewidth of approximately 0.4° at low temperatures is due to disorder, the optical theorem for the transition matrix l_{bb} allows us to estimate the density n of scattering defects. We obtain $n\sigma \approx 0.024$, where σ is the total cross section for scattering out of the bound state by an assumed isolated defect. This is, in fact, not exactly the case, as the defects are associated with boundary zones between domains. Nevertheless, if we ascribe to σ the value $20\text{--}30 \text{ \AA}^2$ as indicated by recent calculations,²⁸ i.e., somewhat smaller than that for a typical adsorbate,²⁹ the cor-

responding density of isolated defects would be $n \approx 1.68 \times 10^{-2}$ per unit cell.

The substantial agreement between experiment and theory demonstrated in this work shows that inelastic exchange with phonons is not the dominant factor in describing the very-low-temperature signature of an elastic resonance, although it does have very measurable consequences. This statement should hold even more for materials with higher Debye temperatures than the metals considered here. In the case of vicinal metal surfaces

it appears to be surface disorder which causes a substantial increase of the FWHM, and, in fact, it is likely that without this disorder the resonance would not be so easy to detect experimentally. This appears to be particularly true for the (113) surface discussed above.

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