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THERMAL ATTENUATION IN RESONANT ATOM–SURFACE SCATTERING

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A method is presented to account for thermal effects in soft potential atom–surface scattering by taking the thermal average of decoupled t-matrix elements. This approach is applied under conditions of resonance. Comparison is made between the calculated and experimental resonance line shapes for 21 meV He atoms incident upon the Cu(113) surface. The calculations show that the specular intensity under resonance conditions has a temperature dependent structure which is different from that away from a resonance. This presently unobserved behavior is discussed.

1. Introduction

Since the 1930's [1], certain He diffraction experiments have shown resonance structures in measurements of diffraction peak intensity as a function of either incident polar or azimuthal angle. The correct interpretation of these results was given by Lennard-Jones and Devonshire [2], who noted that a process they called selective adsorption would take place under certain incident conditions in atom–surface scattering. Selective adsorption continues to be an extremely important method of gaining information about the atom–surface potential [3]. In particular, the bound state energy levels may be deduced from experimental analysis.

The selective adsorption process occurs when a bound state of the potential becomes accessible to an incident particle. This state is actually quasi-bound since it has a finite lifetime. The opening up of this intermediate state gives rise to a resonance behavior in which the relative intensities of backscattered diffracted particles can be strongly affected. Elastic calculations using a hard wall potential have been able to explain the appearance of minima and

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maxima in atom–surface scattering under resonant conditions [4]. Non-hard-wall potentials have also been used to explain such structures [5]. However, neglecting thermal effects in elastic calculations can lead to contradictions with experiment in the line shape of a resonance. Several methods have been introduced to account for inelastic effects. Better agreement with experiment has been achieved using a complex optical potential [6]. More recently, Hutchison [7] proposed a simple method of applying Debye–Waller factors to the scattering amplitudes to account for thermal effects. This approach is an improvement on the purely elastic calculation, but is limited to a hard wall potential [8].

While the corrugated hard wall potential can still be useful in calculations applied to some surfaces such as the alkali-halides, a soft potential is more appropriate for metals. In this paper, a method is proposed for handling thermal effects in resonant atom–surface scattering in the t-matrix formalism. This formalism is particularly well suited to handle the more realistic soft potentials. Application of the method will be made to the case of helium scattering from the surface Cu(113), for which the corrugated Morse potential represents to a good approximation the atom–surface interaction.

2. Theory

The elastic intensities of the diffracted beams may be calculated in the transition matrix formalism using a potential which is divided into two parts: $V = U + v$, where U may be the surface average of V [9]. Then the intensities are calculated from:

$$I_G = \left|\delta_{G,0} - \mathrm{i}mt_{Gi}/\left[\hbar^2(k_{oz}k_{Gz})^{1/2}\right]\right|^2, \tag{1}$$

where

$$t_{Gi} = v_{Gi} + \sum_l v_{Gl}(E_\mathrm{i} - E_l + \mathrm{i}\epsilon)^{-1}\, t_{li}, \tag{2}$$

and v_{pq} are the matrix elements of v taken with respect to the eigenstates of U. E_i is the energy of the incident particle of mass m, and E_l is the particle energy in the lth state. The diffracted particle wavevector component normal to the surface, k_{Gz}, is defined in the standard way $k_{Gz}^2 = k_i^2 - (\boldsymbol{K} + \boldsymbol{G})^2$ where $\boldsymbol{K}$ is the parallel component of the incident wavevector, and $\boldsymbol{G}$ is a reciprocal lattice vector lying in a plane parallel to the surface. The kinematic condition for resonance occurs when $k_{Nz}^2 = -2m|\epsilon_n|/\hbar^2$, where ϵ_n is a bound state energy level of the surface-averaged potential, and N is the reciprocal lattice vector corresponding to the closed resonant channel. Near conditions for resonance, singularities appear in the calculation of t_{Gi}. These are avoided using projection methods in which eq. (2) is written as a pair of coupled integral equations,

only one of which involves the resonant bound states. We consider the case of a single isolated resonance so that

$$t_{Gi} = h_{Gi} + h_{Gb}h_{bi}/(E_i - E_b - h_{bb}), \tag{3a}$$

and

$$h_{pq} = v_{pq} + \sum_l{}' v_{pl}(E_i - E_l + i\epsilon)^{-1} h_{lq}, \tag{3b}$$

where $\sum_l'$ means the summation does not include the resonant bound state. The h_{pq} are calculated by iteration and the diffracted beam intensities can now be evaluated using eq. (3a) even under resonant conditions. These intensities may be written in the form:

$$I_G = I_G^{(0)}|1 - ib/(X - i)|^2, \tag{4}$$

where

$$X = [E_i - E_b - \mathrm{Re}(h_{bb})]/\mathrm{Im}(h_{bb}),$$

and

$$b = N_G h_{Gb} h_{bi}/[(\delta_{G,0} - iN_G h_{Gi})\ \mathrm{Im}(h_{bb})],$$

with $N_G = m/[\hbar^2(k_{iz}k_{Gz})^{1/2}]$ being the density of states for perpendicular motion. $I_G^{(0)}$ is the intensity calculated from eq. (3b) corresponding to a pseudopotential in which the bound state is suppressed. In a plot of I_G as a function of incident angle, the structure of the line shape about a resonance will depend on the value of b. As an example, if $\mathrm{Re}(b)$ is much larger in magnitude than $\mathrm{Im}(b)$, then it is readily seen that the line shape is a minimum for $-2 < \mathrm{Re}(b) < 0$, and a maximum otherwise. Asymmetry in the form of a mixed maximum–minimum structure may appear in the shape of the resonance when $\mathrm{Im}(b)$ is non-negligible. It is known that $\Gamma = -2\ \mathrm{Im}(h_{bb})$ is the energy width of the resonance at half the extremum intensity.

The discussion thus far has involved a summary of how elastic intensities can be calculated at resonance. We now need to introduce thermal effects into the calculations. In an exact approach, the thermal average of t_{Gi} would be used to calculate the diffracted intensities [10]. We shall make the simplifying assumption that we can decouple the amplitudes in eq. (3a) and thermally average them separately. The thermal averaging method used here follows Hutchison's method of scaling scattering amplitudes with Debye–Waller factors, the major difference being the treatment of the denominator of eq. (3a) as discussed below. This decoupling is clearly an approximation the nature of which cannot be properly analyzed in the absence of an exact calculation of the thermal average. However, we note that it reduces to the correct result in the limit of small surface vibrations (the elastic limit), and it gives rise to an overall multiplicative Debye–Waller factor exactly like that observed experimentally on either side of the resonance. The amplitudes h_{Gi}, h_{Gb}, and h_{bi} in

eq. (3a) are thermally attenuated by multiplying them by the factors $\exp(-W_{Gi})$, $\exp(-W_{Gb})$ and $\exp(-W_{\hbar i})$, respectively. The exponent W is given by:

$$W_{pq} = \tfrac{1}{2}(\Delta k_z)^2 \langle u_z^2 \rangle, \tag{5}$$

where $\Delta k_z = k'_{pz} + k'_{qz}$ is the change in perpendicular momentum of the particle from state q to state p calculated in the "Beeby approximation", i.e. $(k'_{pz})^2 = k_{pz}^2 + 2mD/\hbar^2$ with D being the depth of the potential well. The quantity $\langle u_z^2 \rangle$ is the effective, thermally averaged, square displacement of a surface atom in the direction normal to the surface, which involves averaging the motions of several surface atoms.

The scaling method is modified when applied to the amplitude h_{bb}. From the optical theorem, $t - t^\dagger = t^\dagger(G^+ - G^-)t$, the imaginary part of t_{bb} may be related to the probability P_b of a transition from a bound state to the continuum. Thus we have:

$$\mathrm{Im}(t_{bb}) = -(\hbar/2)w_b,$$

where w_b can be viewed as a transition rate from an unperturbed bound state to the continuum. Dividing w_b by the flux of particles in the bound state, $1/\tau_b$, gives the corresponding probability P_b. The term τ_b is a semi-classical quantity which can be estimated in a variety of ways. For example, an approach useful in nuclear resonance theory is to set τ_b equal to the inverse of the energy level spacing of the bound states in the well [11], and this is the method adopted here. An alternative method is to let τ_b be the period of a classical particle moving in the well with energy ϵ_b, and for the potential used below in section 3, these two approaches give values which agree fairly well.

The probability that a bound particle will remain bound is $1 - P_b$, and thermal attenuation is expected to decrease this value. Thus the thermal average of $\mathrm{Im}(t_{bb})$ is taken to be:

$$\langle \mathrm{Im}(t_{bb}) \rangle = -\hbar\left[1 - (1 - P_b)\, \mathrm{e}^{-2W_{bb}}\right]/(2\tau_b),$$

where the thermal attenuation factor is $\exp(-2W_{bb})$ instead of $\exp(-W_{bb})$ since $1 - P_b$ is a probability and not a probability amplitude. Since the operator h obeys the same optical theorem as t, we treat $\langle \mathrm{Im}(h_{bb}) \rangle$ in a similar fashion arriving at the final expression

$$\langle \mathrm{Im}(h_{bb}) \rangle = -\hbar\left\{1 - \left[1 + (2\tau_b/\hbar)\, \mathrm{Im}(h_{bb})\right] \mathrm{e}^{-2W_{bb}}\right\}/(2\tau_b). \tag{6}$$

The quantity $\mathrm{Re}(h_{bb})$ appears only in the equation for X, which is close to zero near a resonance. Any thermal effects upon $\mathrm{Re}(h_{bb})$ will simply shift the angular position of the resonance. Since the magnitude of $\mathrm{Re}(h_{bb})$ is usually small, the temperature dependence of $\mathrm{Re}(h_{bb})$ will be ignored.

The method of treating thermal attenuation as presented here can now be contrasted with the approach of Hutchison [7]. The energy width of the

resonance Γ is given by Hutchison as:

$$F = 2(1 - |S(N, N)|)/(|S(N, N)|\mathrm{d}\delta_N/\mathrm{d}E), \tag{7}$$

where $S(N, N)$ is essentially a scattering amplitude and is scaled by a single Debye–Waller factor $\exp(-W_{NN})$, and δ_N is the phase gained after one period of oscillation in the potential well. In the present paper, Γ is given by $-2\langle \mathrm{Im}(h_{bb})\rangle$ calculated from eq. (6). Clearly both methods show that Γ will increase with temperature. However, the two methods differ in the manner in which thermal effects are introduced into the calculation of Γ.

The value of $\langle u_z^2\rangle$ used in eq. (5) may be obtained for a particular surface and incident particle from experimental data if it exists, and from calculated elastic intensities $I_G^{(c)}$ which agree with the experimental intensities $I_G^{(E)}$ when the latter are extrapolated to zero temperature. Attenuation of elastic beams is found to follow to a good approximation the Debye–Waller form

$$I_G^{(E)} = u_E I_G^{(c)} \exp(-2W_{Gi}), \tag{8}$$

where u_E is the experimental unitarity [12]. From eqs. (5) and (8), $\langle u_z^2\rangle$ may be determined for the particular temperature at which the experiment was performed, regardless of any zero-point motion or anharmonic surface effects. Once $2W_{Gi}$ is calculated from eq. (8), any other $2W_{pq}$ may be determined under the identical incident conditions using the same $\langle u_z^2\rangle$:

$$2W_{pq} = 2W_{Gi}(k'_{pz} + k'_{qz})^2/(k'_{Gz} + k'_{0z})^2. \tag{9}$$

The various transition amplitudes which are used to determine I_G in eq. (4) can now be scaled using the appropriate Debye–Waller factors calculated in the manner described above. The diffracted intensities are still given by eq. (4) with b and X now temperature dependent. We may now see what effects the introduction of thermal attenuation will have on a resonant line shape. For example, if an elastic calculation gives a value of $\mathrm{Re}(b) < -2$ and is much greater in magnitude than $\mathrm{Im}(b)$, then the resonance shape is a maximum. If $b(T)$ then decreases in magnitude with temperature, the resonance changes into a minimum when $b(T)$ becomes greater than -2. The diffracted beam intensity at resonance has a temperature dependence given by:

$$I_G(T) \simeq I_G(0)\, \mathrm{e}^{-2W_{Gi}} \{1 + \mathrm{Re}[b(T)]\}^2. \tag{10}$$

For $\mathrm{Re}[b(T)]$ at $T = 0$ less than -1 and increasing with temperature, eq. (10) shows that $I_G(T)$ will decrease until $\mathrm{Re}[b(T)] \simeq -1$ at some temperature $T_{\min}$ at which $I_G(T)$ will reach a minimum value. As $\mathrm{Re}[b(T)]$ continues to approach zero magnitude for temperatures larger than $T_{\min}$, $\{1 + \mathrm{Re}[b(T)]\}$ will increase from its lower value at $T_{\min}$. This increasing factor is opposed by the factor $\exp(-2W_{Gi})$ leading to the possibility of a relative maximum in the intensity at some temperature $T_{\max} > T_{\min}$. Thus for those resonances, which in an elastic calculation have $\mathrm{Re}(b) < -1$ and $|\mathrm{Re}(b)| \gg |\mathrm{Im}(b)|$, the intensity

measured at resonance as a function of temperature will show structure containing both a minimum and a maximum.

3. Calculations

The method of accounting for thermal effects at resonance described above will now be applied to a particular case, namely the scattering of low energy (21 meV) He atoms from the surface Cu(113). We shall demonstrate the effects of temperature upon the specular beam only. The elastic transition amplitudes are calculated in eq. (3b) by iteration using the corrugated Morse potential:

$$V = D\{\exp[-2\kappa(z - \phi(\boldsymbol{R}))] - 2\exp[-\kappa z]\}, \tag{11}$$

where κ is the range parameter of the interaction potential. The surface corrugation is taken to be one dimensional along the x-axis, and has the form:

$$\phi(x) = da_x \cos(2\pi x/a_x), \tag{12}$$

where $d = 0.016$ and $a_x = 4.227$ Å is the lattice constant for Cu(113). This potential yields elastic intensities which have been shown to agree with experimental intensities extrapolated to zero temperature [3]. Three bound state resonances are observed experimentally in the specular intensity for Cu(113) when the evanescent channel [10] is in resonance with one of the bound states (labeled $n = 0$, 1, or 2) of the surface averaged potential. The specular intensity is calculated from eq. (4) with b and X now temperature dependent. In order to compare with experimental results which were taken at a temperature of 70 K, eq. (8) must be used to determine the Debye–Waller factor, W_{Gi}, because at this temperature zero-point motion is important. Fig. 1 shows the comparison between theory and experiment. Elastic calculations of the specular intensity show narrow maxima rising almost to unity for all three resonances. Thermal effects have changed the signature of each of the three resonances into a broader minimum. The calculated resonance structures for $n = 1,2$ appear at incident angles different from where they appear experimentally because the bound state energies of the Morse potential differ with those of the true potential.

An interesting experiment has been reported by Wesner and Frankl [14] in which a large change in the shape of a resonance as a function of surface temperature is observed for the system He/LiF(001) at low incident energy. In this study, a resonance in the specular beam was initially characterized at $T = 163$ K by a double structure containing a narrow maximum and a broader minimum. As the temperature was increased to $T = 296$ K, the maximum disappeared leaving only the minimum. This is a more complicated situation than that shown in fig. 1 as evidenced by the double structure of the resonance which implies that both the real and imaginary parts of its b function are important.

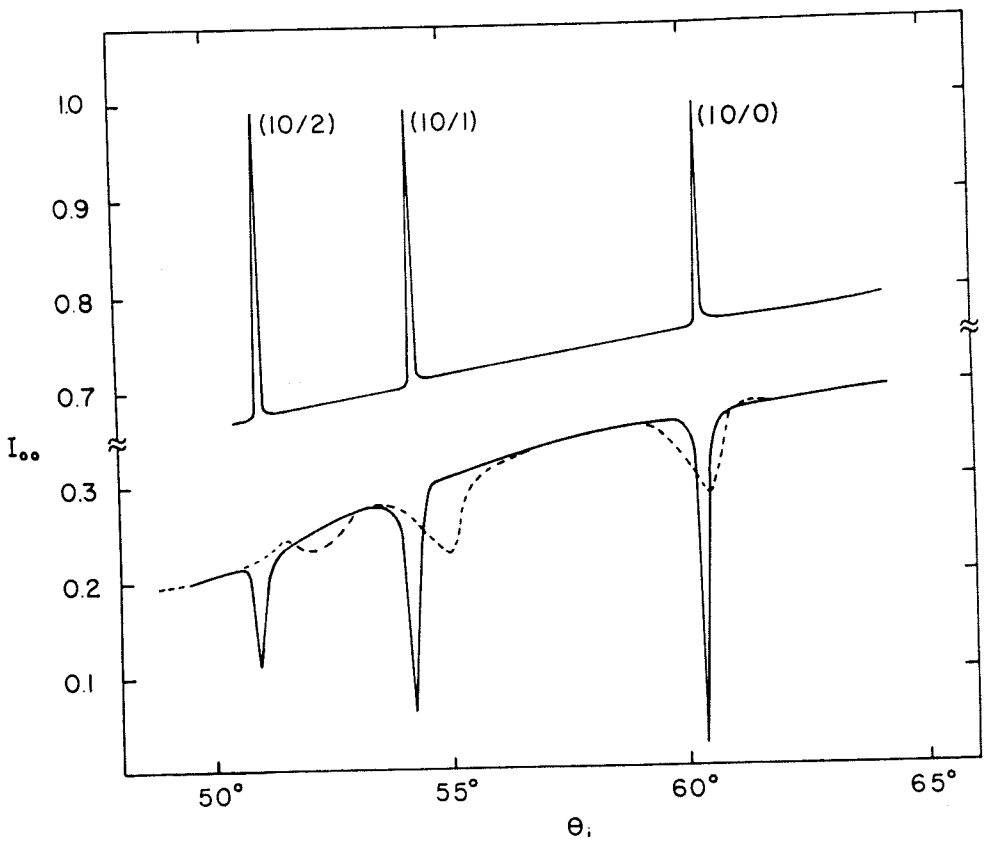

Fig. 1. Specular intensity versus incident angle showing the resonance line shape for He(21 meV)–Cu(113). The solid line showing maxima is the elastic calculation, and the solid line with minima is the present theoretical calculation at a temperature of 70 K. Experimental results taken at $T = 70$ K are shown by the dashed line.

In fig. 2 a detailed comparison with experiment is made for the (10/0) resonance. In this figure, $I(0)$ is the elastic specular intensity which shows a maximum, and $I(T)$ is the specular intensity calculated from eq. (4) and includes thermal effects as described in the previous section. $I_{av}(T)$ demonstrates the effect of angular dispersion in the incident beam on $I(T)$ using the simplest approximation of averaging over the 0.2° experimental angular spread. The experimental resonance structure is wider and not as deep as the calculated line shape. Even after the 0.2° angular dispersion in the incident beam is taken into account, the minimum is still narrower than experiment. An energy dispersion correction was not taken into account, but angular dispersion seems to be the more important of the two effects [13]. It should be noted that additional experimental points may affect the assumed shape of the resonance structure.

When the specular intensity at the bottom of the resonance in the $I(T)$ curve is calculated as a function of temperature, a new structure appears as shown by the curve marked a in fig. 3. A sharp drop in intensity occurs,

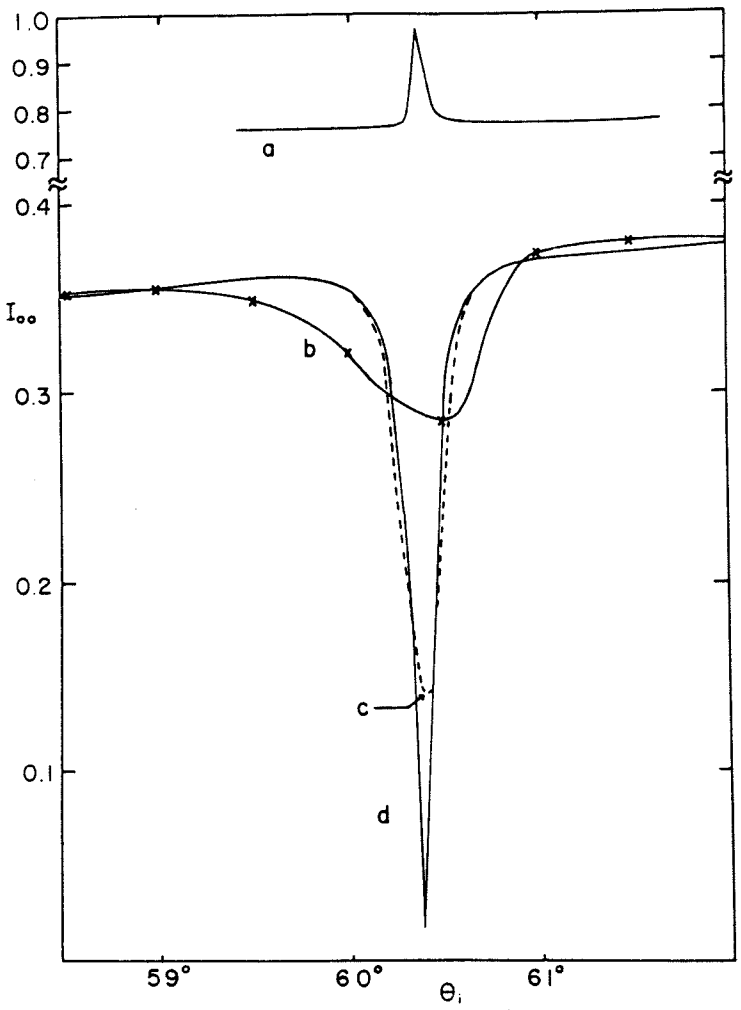

Fig. 2. Detail of the (10/0) resonance of fig. 1: (a) elastic calculation, (b) experiment, (c) present theory with a simple account of the 0.2° angular dispersion, and (d) present theory without angular dispersion.

followed by an increase to a relative maximum. As described qualitatively above, this phenomenon is due to $\mathrm{Re}[(b(T)]$ increasing with temperature from a value less than -1. Assuming no angular spread in the incident beam and sufficiently high temperatures, the intensity can be cast in the form:

$$I = I^{(0)}\, \mathrm{e}^{-aT}\, |1 - b|^2,$$

where $aT = 2W_{Gi}$ and

$$b(T) = b(0)\, P_\mathrm{b}\, \mathrm{e}^{-\alpha T} / \left[1 - (1 - P_\mathrm{b})\, \mathrm{e}^{-\gamma T}\right], \tag{13}$$

with $\alpha T = W_{Gb} + W_{bi} - W_{Gi}$, $\gamma T = 2W_{bb}$, and P_b is the probability defined above in section 2. For the case at hand, α is about an order of magnitude greater than γ. When $|\mathrm{Re}[b(0)]| \gg |\mathrm{Im}[b(0)]|$ the minimum intensity occurs

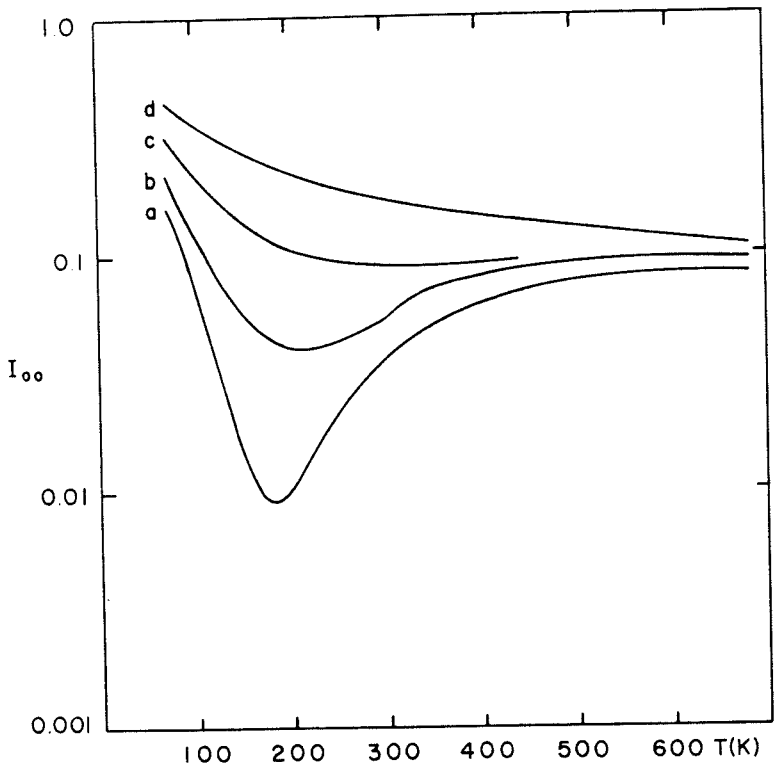

Fig. 3. Specular intensity versus temperature under resonance conditions for the (10/0) resonance of fig. 1: (a) present theory without angular dispersion, (b) with 0.05° angular dispersion, (c) with 0.1° angular dispersion, and (d) with 0.2° angular dispersion.

essentially when $b \simeq -1$ at the temperature T_{min}, and a very good approximate value is:

$$T_{min} = (1 + \mathrm{Re}[b(0)])/(\gamma(1 - 1/P_b)). \tag{14}$$

A good approximation for T_{max} is:

$$T_{max} = P_b\{-\mathrm{Re}[b(0)] - 2 + [-8\mathrm{Re}[b(0)]\gamma(aP_b)]^{1/2}\}/(2\gamma). \tag{15}$$

For all the resonances calculated, these approximate values for T_{min} and T_{max} are good to within 5% and usually even better. The simple forms of eqs. (14) and (15) indicate that a measurement of the structure in the temperature dependent intensities at resonance can give direct information about the assumed behavior of a particle in the bound state.

Fig. 3 also shows the effect of a simple inclusion of incident angular dispersion on the minimum structure. These calculations indicate that the angular dispersion in the incident beam must be less than 0.1° in order for the minimum structure too be clearly observed. However, even if the angular spread is 0.2° or larger there is still a distinct and characteristic difference between the temperature dependence of the intensity at resonance and in an

off-resonance Debye–Waller curve. Fig. 3 shows that for large angular spread, the intensity, while monotonically decreasing with T, has a positive curvature. The experimentally measured Debye–Waller curves over the same temperature range give straight lines or negative curvatures.

Finally, it should be noted from fig. 1 that outside of a resonance, the calculated and experimental curves agree well with each other. Away from a resonance, the specular intensity does not exhibit the temperature dependent structure depicted in fig. 3, but follows the usual Debye–Waller effect form.

4. Conclusions

We have presented a method of introducing thermal effects through Debye–Waller factors into calculations of diffracted beam intensities under conditions of resonance. These effects are able to change narrow, elastic maxima into broader minima. It is found that the resonance line shape has the same minimum structure as observed in experiment, and possesses asymmetry. However, the calculated line shape shows a resonance structure which is deeper and not as wide as that measured by experiment. In addition, a new structure is observed when the diffracted intensity at or very close to a resonance is calculated as a function of temperature. If this structure is to be observed experimentally, it appears to be important for the incident beam to be very well collimated.

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