the fluctuations in the (001) plane by the piezo-electric coupling modifies the critical properties to those given by mean field theory without loga-rithmic correlations.[12] The piezoelectric coupling must therefore be included in any detailed com-parison between experiment and theory for the critical properties of these materials.

Finally, asymmetric quasielastic critical scat-tering such as that shown in Figs. 1–3 is to be ex-pected at other continuous phase transitions where the order parameter is linearly coupled to an acoustic mode and where both the order parame-ter and the acoustic mode can give rise to scat-tering. Examples other than ferroelectrics which are piezoelectric in the paraelectric phase are the rare-earth vanadates,[13] such as $TbVO_4$ and $DyVO_4$. It would be of interest to examine these systems in detail especially as dynamical effects may play a more important role than in DKDP.

I am grateful to the authors of Ref. 2 for discus-sions and permission to reproduce their results.

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Angular Dependence of Oscillatory Structure in Low-Energy Ion-Surface Scattering

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Measurements have been performed of the dependence on scattering angle and tar-get orientation of the oscillatory structure recently observed in low-energy ion scatter-ing from surfaces. Wide variation is exhibited in the behavior of oscillation maxima as a function of scattering angle depending on the target species studied. A semiquantita-tive model is presented which treats the phenomenon in terms of quantum mechanical phase interference between pairs of near-resonant quasimolecular levels.

We present results of an experimental and theo-retical study of the mechanism responsible for the dramatic oscillatory behavior recently observed by Erickson and Smith[1] in the yield of He^+ ions scattered from surfaces. We have performed measurements of the dependence on scattering an-gle θ and target orientation ψ of the location of oscillation maxima.[2] These experiments provide critical new information about the ion-surface in-teraction, and strongly support the view that the oscillatory behavior arises from quantum me-chanical interference between near-resonant ion-
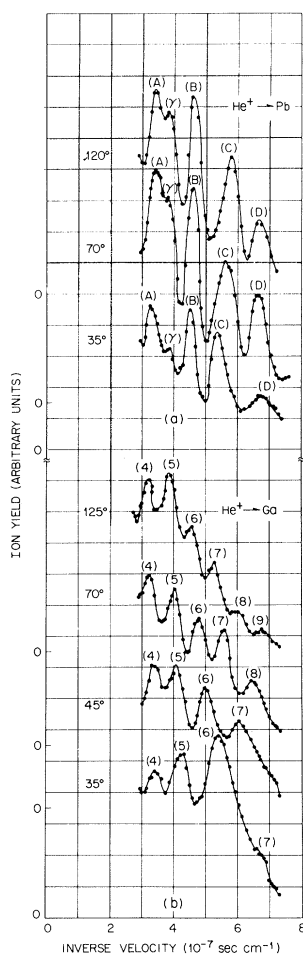
FIG. 1. Relative intensity of scattered He⁺ ions versus the inverse of the initial velocity, for several scattering angles θ. (a) Pb target; (b) GaP target (Ga surface peak).

FIG. 2. Schematic illustration of near-resonant charge-exchange model.

ic and neutral levels. We present a semiquantitative model based on this picture which accounts for the positions and spacings of oscillation peaks, and for the distinctive angular dependence observed.

The apparatus consists of an ion source, electrostatic focusing lenses, a Wien filter, a target chamber, and an electrostatic analyzer able to move through laboratory scattering angles ranging from 20° to 135°. The pressure in the target chamber was typically 2×10^{-8} Torr. Ion yields, normalized to integrated beam current, were obtained by sweeping the electrostatic analyzer over the entire energy range of scattered ions and extracting the peak intensity at the energy corresponding to binary collision with the specified surface atom.
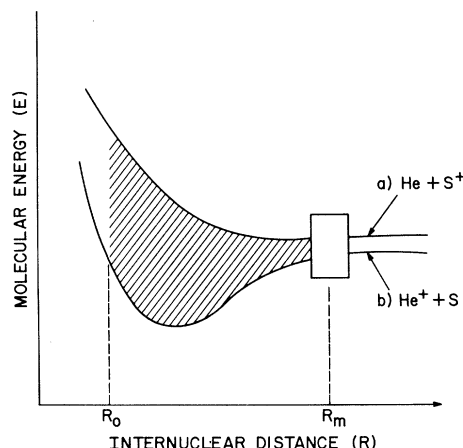
Detailed measurements have been performed of the scattering of 200–3000-eV He⁺ ions by Pb and GaP targets. We note three major observations: (1) As shown in Fig. 1, the intensity of scattered He⁺ oscillates as a function of incident energy. For the same system and same scattering angle, our results agree closely (although not exactly) with those of other groups.[1,3,4] (2) Our measurements show no observable shifts in the positions of oscillation maxima for both Pb and Ga (in GaP) for target orientation angles ψ ranging from 110° to 180°. The oscillatory structure changes markedly as the scattering angle θ is changed (see Fig. 1). Furthermore, these changes depend on the nature of the target species; Ga peaks shift to lower energy as θ is decreased, whereas Pb peaks shift mostly in the opposite direction.

Most of the observations can be understood within the framework of the model illustrated schematically in Fig. 2. Situations where the presence of a pair of closely lying quasimolecular states in interference lead to oscillations in total or differential cross sections are familiar in the field of gas-phase ion-atom collisions.[5] In the present case the two states correspond to an He⁺ ion in the vicinity of a neutral surface atom S (curve b) and a neutral He atom in the vicinity of surface atom S⁺ which is missing an electron from a level nearly resonant with the ionization potential of He (curve a). This picture is strongly supported by the fact that regular oscillatory behavior has been observed only for target species with d-state energy levels lying within 10 eV of the He ionization potential, 24.6 eV.[1,3] We hypothesize that at an internuclear separa-

tion $R \simeq R_m$ a coherent mixing of the two levels occurs because of the exchange (charge-transfer) interaction. As the collision evolves, a differential phase $\Delta \varphi$ develops between the two paths, on both the incoming and outgoing legs, until the mixing region is traversed again. The intensities I_+ and I_0 of scattered ions and neutral atoms are determined by the total accumulation of differential phase[5]:

$$I_+ = \alpha_+ + \beta \cos^2(\Delta \varphi/2),$$
$$I_0 = \alpha_0 + \beta \sin^2(\Delta \varphi/2). \tag{1}$$

The coefficients α_+, α_0, and β are slowly varying functions of incident ion energy which include damping effects due to other neutralization processes and to the finite width of the surface d level. Thus the ion intensity will exhibit maxima whenever the condition $\Delta \varphi = 2\pi n$ is met. The phase $\Delta \varphi$ is given by

$$\Delta \varphi = \frac{1}{\hbar} \int \Delta E(t) dt = \frac{1}{\hbar} \int \frac{\Delta E(\vec{R})}{v(\vec{R})} d\vec{R}, \tag{2}$$

where the integral is evaluated along the trajectory from the initial to the final crossing of the mixing region at R_m. $v(\vec{R})$ is the instantaneous component of velocity tangent to the trajectory, and ΔE is the splitting between curves a and b of Fig. 2.

Equations (1) and (2) provide a basis for analysis of our experimental results. Note first that, at least at high energies where velocity is most nearly constant over the path of integration, Eq. (2) can be approximated as

$$\Delta \varphi \simeq (2/\hbar v) \int_{R_0}^{R_m} \Delta E(R) dR = (2/\hbar v)\langle ER \rangle. \tag{3}$$

R_0 is the turning point, and the factor of 2 arises from inclusion of both incoming and outgoing legs. Thus the oscillation peaks should be approximately equally spaced when plotted versus inverse relative velocity, $1/v$. As can be seen from Fig. 1, although there is some deviation, this is nearly the case except for the one He^+-Pb peak labeled γ in Fig. 1. The existence of this peak may be associated with the fact that there are two different d levels in Pb lying within a few eV of the He ionization potential.

Using Eq. (3), we can obtain an experimental measure of the quantity $\langle ER \rangle$. We extract from Fig. 1 the values 17.7 and 23.5 eV Å for He^+ on Pb and GaP, respectively. These numbers are consistent with the values 22 eV Å for He^+-Pb and 19 eV Å for He^+-Ga estimated by a simple

calculation.[6]

In order to employ the model to account for angular distributions, it is necessary to specify more completely the quantities in Eq. (2). There are two extremes in which this task is simplified. The first extreme occurs if the ion-surface interaction is invariant to motion along the surface, and depends only on the distance $R_\perp$ between the ion and the surface. The velocity v in Eq. (2) then refers to the component of velocity normal to the surface, and R_m defines a plane parallel to the surface. In this limit there would be a very strong, predictable shift of oscillation peaks depending both on the scattering angle θ and the target orientation ψ. The fact that we see no variation with ψ whatever and a very different dependence on θ from that predicted effectively rules out this limiting case.

The second and more realistic extreme is the ion-atom limit in which the ion interacts with only the particular surface atom from which it scatters. The mixing distance R_m then defines a sphere surrounding the surface atom, and the velocity appropriate to Eq. (2) is the radial velocity v_r. This model predicts that (a) the results will be independent of target orientation ψ, in agreement with experiment and (b) the θ dependence is determined both by the amount of time spent in the phase development region and by the amount of phase area $\langle ER \rangle$ swept out during the collision. We can rewrite Eq. (2) in the form

$$\Delta \varphi = \frac{2m}{\hbar} \int_{R_0}^{R_m} \frac{\Delta E(R) dR}{\{2m[E - V(R)] - L^2/R^2\}^{1/2}}, \tag{4}$$

where $V(R)$ is the effective ion-atom potential, E is the initial energy, and L and m are the angular momentum and reduced mass of the ion-atom pair. L is related to the final scattering angle θ through the well-known classical deflection function,

$$\theta = \pi - 2L \int_{R_0}^{\infty} \frac{dR}{R^2\{2m[E-V] - L^2/R^2\}^{1,2}}, \tag{5}$$

The solid curves of Fig. 3(b) are calculated from Eqs. (4) and (5), assuming ΔE to be constant for $R < R_m$ and $V(R)$ to be of the form Ze^2/R. The best-fit values of ΔE and Z are 8.8 eV and 25. Even using these vastly over-simplified forms for ΔE and V, the model is able to account satisfactorily for the angular dependence and the deviation from equal peak spacing in the He^+-GaP results. The He^+-Pb results cannot be satisfactorily fitted using constant ΔE and the Coulomb potential. This can perhaps be understood from the
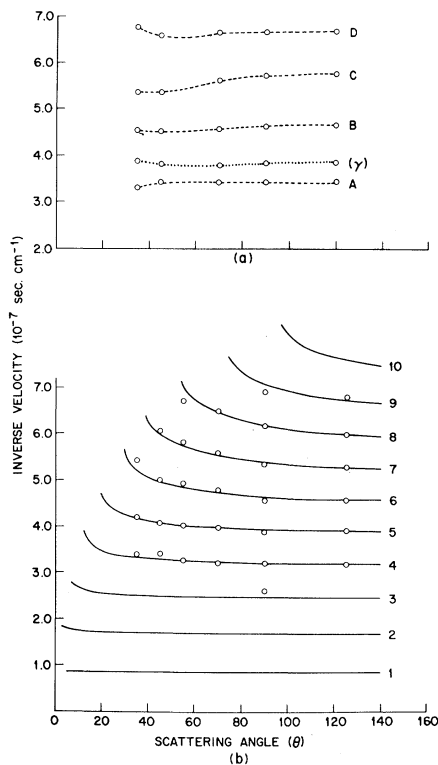
FIG. 3. Angular dependence of peak positions. Points are experimental. (a) He^+-Pb; peaks are lettered arbitrarily. (b) He^+-GaP; peaks are labeled by phase index $n = \Delta\varphi/2\pi$. The solid curves are theoretical.

calculations of Ref. 6, which indicate that because a $5d$ orbital is involved, ΔE reaches a maximum at relatively large R for He^+-Pb, and is very small near the turning point R_0. Thus $\langle ER \rangle$ is insensitive to small changes in R_0, and peaks should shift to lower values of $1/v$ as θ is decreased for large θ; i.e., the constant-ΔE approximation is unsatisfactory for the He^+-Pb system.

The oscillatory behavior observed in low-ener-

gy ion-surface scattering represents a classic example of quantum mechanical phase interference arising from the principle of superposition. Our measurements of the angular dependence of oscillation maxima constitute strong evidence that the phenomenon arises from near-resonant charge exchange associated with a specific ion-atom interaction. Nevertheless, the electronic potentials involved are profoundly influenced by the nature and proximity of neighboring surface and bulk atoms. Since the positions and angular dependences of oscillation peaks are seen to depend sensitively on these interaction potentials, and since the differential phase $\Delta\varphi$ can be routinely measured to better than 1% accuracy, angular-dependent ion-surface scattering appears promising as a probe of surface electronic structure.

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