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Oscillatory Cross Sections in Low-Energy Ion Scattering from Surfaces

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Oscillations in the low-energy noble-gas ion-scattering cross sections versus primary ion energy have been observed for a number of solid surfaces. This behavior is ascribed to resonant electron exchange between electronic states of the surface atom and the primary ion. The oscillations are sensitive to the particular electronic energy levels and to the chemical environment of the surface atom.

Ion-scattering spectrometry (ISS) has been shown to give direct information about the identity of atoms on a solid surface.¹⁻³ This technique involves bombarding a surface with low-energy noble-gas ions and detecting those scattered ions which have undergone binary elastic collisions with surface atoms. Such collisions result in scattered ions having energies characteristic of the surface atoms involved in the collision, allowing an identification of these surface atoms. However, quantitative analysis of these surface constituents requires additional information on the ion-scattering cross sections for each element.

Ion-scattering cross sections versus primary ion energy were, therefore, measured by bombarding a target surface at an angle of 45° with noble-gas ions and detecting the ions scattered through a laboratory angle of 90°. Ion yields were obtained by tuning the electrostatic energy analyzer to the peak associated with the element of interest and measuring the scattered ion current. Yield data were corrected for variations in primary ion current and energy-analyzer transmissivity.

In making these measurements, fine structure has been discovered for a number of elements. This structure is observed as an oscillation of the ISS yield versus primary energy. Each of the elements having such behavior has shown a unique pattern in the oscillation spacings. Two examples are shown in Fig. 1 for the cases of ${}^4\text{He}^+$ ions scattered from a Pb foil and a Ge crystal. Although He^+ ions were used for most of the experimental work, both Ne^+ and Ar^+ ions have been shown to produce similar structure in the ion-yield curves.

Similar oscillations are known to exist for ionic collisions in gases⁴; however, this is the first time they have been observed for ion scattering from surfaces. These data demonstrate that previous concepts,⁵ explaining the cross-section curves as smoothly varying with a single maximum, have to be modified for ion scattering from surfaces.

These oscillations are ascribed to electron exchange processes in which an electron from the target atom neutralizes the scattered primary ion. In a simplified model of charge-exchange collisions, the incident ion and the surface atom

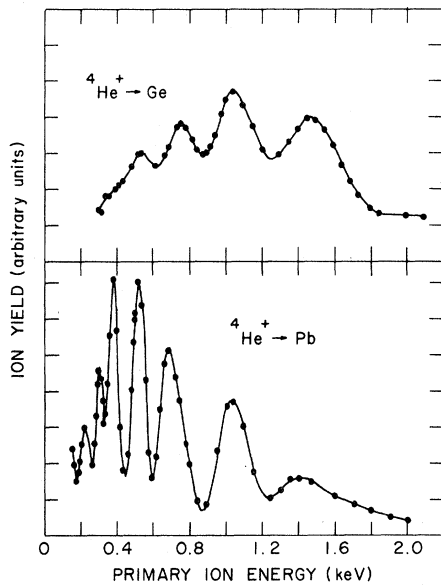


FIG. 1. ISS yield versus primary ion energy for $^4\text{He}^+$ scattering from Ge and Pb targets.

are considered to form a quasimolecular state while in close proximity. During this brief encounter ($\sim 10^{-16}$ sec), the electrons initially orbiting their respective nuclei now orbit about both nuclei. With the electrons being shared during the collision, it is possible for the incident ion to capture one of the electrons of the surface atom as it scatters away. When this happens, the neutralization of the scattered ion results in a decrease in the detected ion yield.

Such electron-exchange processes are dependent upon the interaction time, which is a function of the primary ion velocity. A sufficiently large ion velocity will produce a collision time so short that the electron has just enough time to transfer to the incident ion; the ion then scatters away neutralized. For a somewhat lower ion velocity (and longer collision time) there will be sufficient time for the electron to transfer to the incident ion and back again to its parent atom, resulting in no neutralization. For progressively lower ion velocities, a succession of electron-exchange events may take place. This velocity dependence causes the scattered-ion yield to have minima at those ion velocities (collision times) where charge exchange results in the scattering of a neutral.

To test whether the cross-section structure was velocity dependent, experiments using both

$^3\text{He}^+$ and $^4\text{He}^+$ ions were conducted. The oscillatory structure for both cases was the same when scaled in energy to account for mass differences. This is consistent with our proposed resonant charge-exchange mechanism.

Lichten⁶ has shown that for asymmetric charge-exchange collisions, i.e., $A+B^+ \rightarrow A^+ + B$, a condition for quasiresonant charge exchange is that the initial-state and final-state electronic energies be nearly degenerate. This condition appears to be borne out by our measurements, since those elements (Ga, Ge, In, Sn, Sb, Pb, Bi) exhibiting oscillatory structure have d -electron energy levels within 10 eV of the He first ionization energy (24.6 eV). Elements (Al, Si, Ag, Cd, Cu, As) with greater energy separation have shown no observable structure. Specifically, it is suggested that the He $1s$ level is filled by an electron from the Ge $3d$ and Pb $5d$ levels for the two cases shown in Fig. 1.

While the ISS yield curves of Fig. 1 display rather regular oscillatory behavior, this is not true of all the elements examined. For example, $^4\text{He}^+$ scattering from Bi results in the yield curve shown in Fig. 2. Measurements made on our laboratory apparatus and on a commercial ISS system⁷ yielded identical results. Other elements have also shown reproducible amplitude variations in addition to their particular oscillation spacings. These amplitude variations appear to be characteristic of these particular elements. An analytical application of this new phenomenon

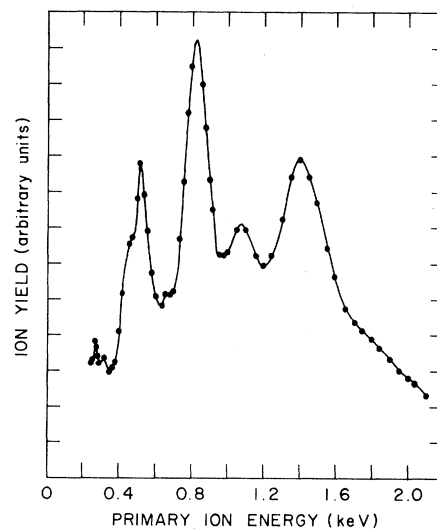


FIG. 2. ISS yield versus primary ion energy for $^4\text{He}^+$ scattering from Bi, illustrating nonregular oscillatory behavior.

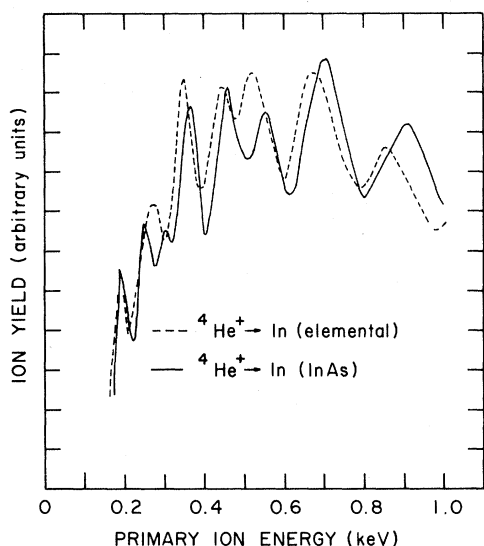


FIG. 3. Comparison of the In (elemental) and In (InAs) ISS yields for $^4\text{He}^+$ primary ions. The In (InAs) curve has been doubled in amplitude for comparative purposes.

is suggested by comparison of the yield curves for Pb (Fig. 1) and Bi (Fig. 2). Ion scattering from these two elements cannot be resolved by normal ISS techniques because of their small mass difference. However, they may be resolved on the basis of their significantly different yield curves.

Comparisons were made between data for target atoms in elemental form and in compound

form. For example, Fig. 3 compares the scattered-ion yield from In atoms in elemental In with that from In atoms in an InAs crystal. Clear differences exist between the two cases, especially in the extrema spacings and number of oscillations. These data suggest the possibility of using modified ISS techniques to examine changes in electronic energy states due to chemical binding of atoms at the surface of a solid.

Besides the analytical potential of this phenomenon, these observations demonstrate that ISS techniques can provide a method for investigating fundamental collision processes on a wide variety of elements in solid-state form.

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⁴F. P. Ziemba and E. Everhart, *Phys. Rev. Lett.* **2**, 299 (1959); W. C. Keever and E. Everhart, *Phys. Rev.* **150**, 43 (1966), and references cited; J. Perel, R. H. Vernon, and H. L. Daley, *Phys. Rev.* **138**, A937 (1956); J. Perel, H. L. Daley, and F. J. Smith, *Phys. Rev. A* **1**, 1626 (1970); T. A. Green, in *Energy, Structure, and Reactivity: Proceedings. Boulder Summer Research Conference on Theoretical Chemistry*, edited by D. W. Smith and W. B. McRae (Wiley, New York, 1973).

⁵See Fig. 9 of Ref. 2 and accompanying discussion.

⁶W. Lichten, *Phys. Rev.* **139**, A27 (1965).

⁷3M brand Ion-Scattering Spectrometer, Model 520.