resonance structure. In this case there will be a nonzero width to the collective state. These arguments may be paraphrased by the statement that the addition of an absorptive band which changes rapidly enough will give rise to an additional collective mode.

By using an effective mass approximation and a constant dipole moment, the interband contribution to the imaginary part of the polarizability [Eq. (32)] may be calculated. As long as the density of states at one of the ends of the two bands being considered does not go to zero continuously, Im P will have a discontinuous jump. By choosing alternative simple band schemes one may reproduce practically any behavior of Im P desired. Although parameters may be adjusted in the band scheme to agree with the observed energy losses, the test of the model is, of course, one that also predicts other physical properties unrelated to the energy losses by invariance arguments.

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Sputtering Experiments in the Rutherford Collision Region*

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Sputtering experiments have been conducted by bombarding the (110) plane and the (100) plane of single crystals of copper by deuterons incident normally with energies from 0.8 to 2.5 Mev from a Van de Graaff accelerator. Electron micrographs showed that surface etch pits were formed by bombardment, even at these high energies. Measurements of optical transmission of the sputtered film collected on a quartz tube indicated a deviation from a cosine distribution in the energy range investigated. For 800-kev deuterons bombarding a (100) plane in Cu, the absolute value of the sputtering ratio was $S=1.1\times10^{-3}$ atom/ion at 25° with respect to the surface normal and 5.8×10^{-4} at angles larger than 40°; and $S<0.9\times10^{-3}$ atom/ion at 25° for 1.5-Mev deuterons. For 0.80- and 2.5-Mev deuterons bombarding a (110) plane, $S<5\times10^{-2}$ atom/ion. These data agree with the calculations of Goldman and Simon and of Pease within a factor of 2, but disagree with those reported by Pleshivtsev by 2 to 4 orders of magnitude. The sputtering ratio was found to decrease with increasing ion energy, in qualitative agreement with the theoretical predictions but contrary to the findings of Pleshivtsev.

SPUTTERING phenomena have been studied by many authors[1] in the hard-sphere collision region and to a lesser extent in the region of weakly screened Coulomb collisions. For the energy region above 100 kev where for light incident ions ($Z_1\leqslant 2$) bombarding targets with $Z_2<40$ the Rutherford scattering predominates, the only data for "back" sputtering[2] known to the author are preliminary results reported by Pleshivtsev.[3] However there exists a discrepancy of 3 to 4 orders of magnitude between sputtering ratios reported by this author for deuterons bombarding a copper target and the theoretical predictions for the same system, such as those of Goldman and Simon,[4] Goldman, Harrison, and Coveyou,[5] Harrison,[6] and Pease.[7] It seemed interesting, therefore, to check the experimental result by experiments in the Rutherford collision region. Such collisions, which displace target atoms, occur when the energy E of the incident ions is greater than a limiting energy[8]

$$E_B=4E_R^2Z_1^2Z_2^2(Z_1^{\frac{2}{3}}+Z_2^{\frac{2}{3}})\frac{M_1}{M_2}\frac{1}{E_d}, \tag{1}$$

where M_1, Z_1 and M_2, Z_2 are the mass and the atomic number of the incident ion and the target atom, respectively, $E_R=13.6$ ev is the Rydberg energy for hydrogen, and E_d is the energy required to displace an atom from its lattice site. For many metals the values

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* Work performed under the auspices of the U. S. Atomic Energy Commission.

[1] M. Kaminsky, review article for Ergeb. exakt. Naturwiss. (to be published). For data up to 1955, see the article by G. K. Wehner, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7, p. 289.

[2] It is necessary to discriminate between "back" and "forward" sputtering. In "back" sputtering the target particles leave from the surface that is struck by the incident ion beam, while in "forward" sputtering they leave from the opposite surface [see experiments by M. W. Thompson, Phil. Mag. 4, 139 (1959)].

[3] N. V. Pleshivtsev, Soviet Phys.—JETP **37**, 882 (1960).

[4] D. T. Goldman and A. Simon, Phys. Rev. **111**, 383 (1958).

[5] D. T. Goldman, D. E. Harrison, and R. R. Coveyou, Oak Ridge National Laboratory Report 2729, 1959 (unpublished).

[6] D. E. Harrison, J. Chem. Phys. **32**, 1332 (1960).

[7] R. S. Pease, Rend. S.I.F., **XIII** 158 (1959).

[8] N. Bohr, Kgl. Danske Videnskab. Selskab Mat.-fys. Medd. **18**, 8 (1948).

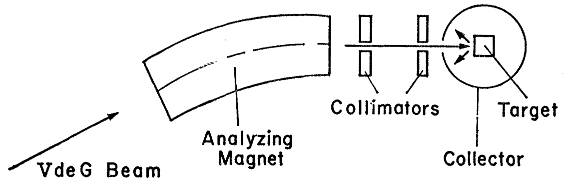

FIG. 1. Schematic diagram of the experimental arrangement.

of E_d are 20–25 ev (e.g., $E_d=25$ ev for Cu and 21 ev for Ag).

In our experiments two single crystals of electrolytic copper, $\frac{1}{4}$- $\times\frac{1}{4}$- $\times$1-in., were bombarded under normal incidence with deuterons with energies of 0.8—2.5 Mev. The surface bombarded was the (110) plane of one crystal and the (100) plane of the other. These crystallographic planes were parallel within 3° to the actual target plane, as determined by Laue diagrams. In a cycle, repeated three times, the surfaces were polished mechanically and very slightly etched. The surfaces obtained had a mirror finish and were examined by optical and electron microscopy before and after the bombardment. The appearance of pits in the surface could be observed after the bombardment. The results of such surface "etch effects" will be reported elsewhere. Before the crystal was mounted in the target holder, the surface was freed of adherent traces of the replicating plastic by swabbing with trichlor ethylene, acetone, and methyl alcohol. The target chamber shown schematically in Fig. 1 was fitted with a triple-bellows system by which the crystal could be rotated around an axis parallel to the surface plane under bombardment, and moved horizontally and vertically in a plane perpendicular to the direction of the incident beam. With this arrangement the sputtering can be studied as a function of the angle of incidence and a fresh target spot can be bombarded in each run. Around the target was a collector consisting of a quartz tube with an inner diameter of 18 mm and a length of 100 mm. In order to pass the incident beam, a slit about 3 mm wide and parallel to the axis of the tube was cut down the full length. Another bellows system allowed the collector to be shifted parallel to the axis of rotation of the crystal. This exposed a fresh collector surface for each sputtering experiment without opening the machine.

A beam of deuterons from a Van de Graaff passed through an analyzing magnet and two collimating plates before striking a target spot about 2 mm in diameter. The current densities for different runs ranged between 300 and 600 μa/cm^2. The measured total target current was corrected for the secondary electron current in order to determine the actual beam current. The secondary electrons made up about 10% of the total current, the contribution at 2.0 Mev being about 25% less than at 0.8 Mev. Aarset, Cloud, and Trump[9] have observed a similar variation of the secondary emission from Ni and Au bombarded by protons, but their secondary currents were considerably larger than in the present experiments.

The vacuum in the target chamber was held at 2×10^{-7} mm Hg. The sputtered target atoms were condensed on the quartz wall. The relative thickness of the deposits was measured by an optical transmission method using a monochromatic light source (sodium vapor lamp), a sapphire light pipe, and a photomultiplier arrangement. The relationship between the transparency of the deposits and the layer thickness was taken from Koedam's data.[10] A layer 30 Å thick is still detectable. A mass spectrometer now under construction will serve as a more sensitive detector and will distinguish the different species of sputtered particles (ions, atoms, or molecular species). However, the deposition of the sputtered particles on a transparent collector has the advantage of showing their angular distribution.

Our measurements indicate that the angular distribution does not follow a cosine law but is more peaked in the direction normal to the surface, and approaches the cosine distribution only for angles larger than 40° from this normal. The deposit appeared to show a faint spot pattern corresponding to the preferred ejection of atoms along close-packed crystal directions. In the case of the (100) crystal plane, the contribution of the [110] directions seemed to show up under 45° but was too thin for a definite identification. Because of the width of the slit in the collector and the diffraction effects at the edges of the slit, the deposits could be detected accurately only for angles larger than 25° with respect to the normal.

The observed deviations from the cosine distribution do not allow the determination of a "uniform" sputtering ratio. The first exploratory experiments were conducted by bombarding a (110) plane of a copper single crystal successively with 0.80- and 2.5-Mev deuterons. The chosen period of irradiation was too short to allow more than an upper limit $S_{\max}=5\times10^{-2}$ to be set for the sputtering ratio at each energy. Since these results indicated a ratio approximately two orders of magnitude lower than Pleshivtsev's, an absolute value for the sputtering ratio was sought. For 800-kev deuterons bombarding a (100) plane of a copper single crystal, the sputtering ratio was found to be $S=1.1\times10^{-3}$ atom/ion at 25° and 5.8×10^{-4} atom/ion at angles larger than 40°. The results at these two angles are shown in Fig. 2 as two dots connected by a solid line. For the case of 1.5-Mev deuterons bombarding the same single-crystal plane, the limited irradiation time allowed establishing only an upper limit $S_{\max}=0.9\times10^{-3}$ atom/ion. As shown in Fig. 2, these values of the sputtering ratios are 3 to 4 orders of magnitude smaller than those reported by Pleshivtsev. The present results indicate

[9] B. Aarset, R. W. Cloud, and J. G. Trump, J. Appl. Phys. 25, 1365 (1954).

[10] M. Koedam, thesis, State University of Utrecht, 1961 (unpublished).

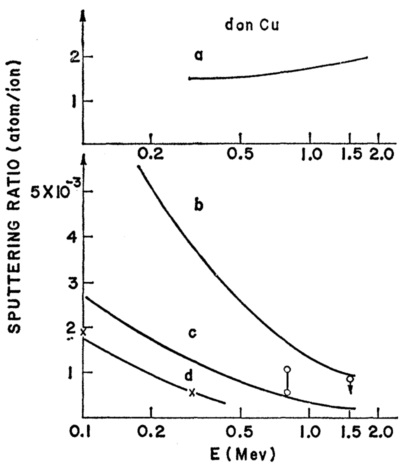

FIG. 2. Comparison of sputtering ratios for deuterons bombarding copper under normal incidence. Curves a, b, c, and d represent the values from references 3, 7, 4, and 5, respectively. The points marked × in curve d are from reference 6. The two open circles connected by a solid line represent the values determined from the deposits collected at angles of 25° ($S=1.1\times10^{-3}$) and larger than 40° ($S=5.8\times10^{-4}$) when the (100) plane of a copper single crystal was bombarded with 0.8-Mev deuterons. The established upper limit of the sputtering ratio for 1.5-Mev deuterons is also shown by an open circle.

also that the sputtering ratio decreases with increasing energy, contrary to the findings of Pleshivtsev. Unfortunately, Pleshivtsev did not state the experimental conditions under which he obtained his results. However, the high values of the sputtering ratio and their increase with increasing energy seem to indicate that an evaporation process is superimposed on the sputtering process. Such target evaporation becomes likely if the power transmitted by a high-energy beam at large ion currents is too great to be dissipated rapidly enough by a thin target (e.g., a foil or film).

It seems of interest to compare the present results with values calculated on the basis of different theoretical concepts and to discuss briefly a sputtering model which seems to be plausible for the energy region considered. Consider a Rutherford collision in which an incident particle penetrates the target where its mean free path is λ (about 0.8×10^{-4} cm for 500-kev deuterons on Cu) and displaces a target atom from its lattice site as a "primary knock-on." The cross section σ_d for such collisions for $E>E_B$ has been given by Bohr[8] as

$$\sigma_d=4\frac{M_1}{M_2}Z_1^2Z_2^2E_R^2\left(1-\frac{E_d}{\Lambda E}\right)\frac{\pi a_0^2}{E_dE}, \tag{2}$$

where $\Lambda=4M_1M_2/(M_1+M_2)^2$ and a_0 is the Bohr radius. The mean energy $\bar{E}$ of these "primary knock-ons" is

$$\bar{E}=E_d\ln(E_{\max}/E_d), \tag{3}$$

with

$$E_{\max}=\frac{4M_1M_2}{(M_1+M_2)^2}E.$$

If the condition $\bar{E}\ll E_{\max}$ is fulfilled, the primary knock-ons are displaced normal to the direction of incidence. These primary knock-ons in turn interact with neighboring lattice atoms by hard-sphere collisions and produce secondary displacements. Such successive collisions continue until the displaced atoms have cooled to such an extent that their kinetic energies have fallen to the order of the displacement energy. A certain fraction of these displaced particles will have a chance to reach the surface and to escape. Several authors tried, on the basis of different concepts, to relate the number of sputtered atoms to the number of such displaced target atoms. Certain simplifying assumptions are commonly made in all these theories. For instance the anisotropy of the energy transfer within the lattice is neglected, as is the electron excitation as a principal mode of energy loss for fast-moving charged particles in a solid [whenever $E>E_c=\frac{1}{16}(M_1/m_e)W_i$, where W_i is the Fermi energy of the free electrons and m_e is the electron mass.] For d on Cu, $E_c=1.1$ kev. As long as $\bar{E}<E_c$, this effect will be important only for the energy loss of the incident particle.

Goldman and Simon[4] assumed that the production of primary knock-ons is inversely proportional to the mean free path λ of the incident particle. The sputtering ratio S was assumed to be also proportional to the average number $\bar{\nu}$ of displaced secondary atoms and, under simplified assumptions, corrections were made for displaced target atoms which got trapped in the lattice. According to the authors, the expression for the sputtering ratio S is

$$S=0.17\bar{\nu}\frac{Z_1^2Z_2^2e^4}{EE_dR^2}\frac{M_1}{M_2}\frac{1}{\cos\psi}, \tag{4}$$

where [11] $\bar{\nu}=[0.885+0.561\ln\frac{1}{4}(x+1)](x+1)/x$, with

$$x=\frac{4M_1M_2}{(M_1+M_2)^2}\frac{E}{E_d}.$$

Here ψ is the angle of incidence and the other notations are the same as used in Eqs. (1)–(3). Calculated values for $S(E)$, based on Eq. (4) for a copper target bombarded by deuterons, are plotted as curve *c* in Fig. 2.

Applying the same model, Goldman, Harrison, and Coveyou[5] performed a Monte Carlo calculation and obtained the results shown as dots in curve *d* in Fig. 2. A comparison between curves *c* and *d* shows a qualitative agreement for the function $S(E)$, but quantitatively the sputtering ratios plotted in curve d are smaller than those in curve c.

Harrison[6] used a modified model to derive an analytical expression which includes the equation of Goldman and Simon as a special case. The sputtering ratios

[11] F. Seitz and J. Koehler in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 307.

calculated from Harrison's theory are also shown on curve d of Fig. 2.

According to Pease,[7] the sputtering ratio S is determined by three factors. One is the effective collision area available within one layer ($S \propto \sigma_d n^{\frac{2}{3}}$); the second is the number of layers contributing to sputtering ($S \propto 1+N^{\frac{1}{2}}$); the third is the total number of displaced atoms per primary knock-on ($S \propto \frac{1}{2}\bar{E}/2E_d$). Thus the sputtering ratio for normal incidence and for $2E_d < \bar{E} < E_{\max}$ is given by

$$S=\sigma_d n^{\frac{2}{3}}(1+N^{\frac{1}{2}})\times\tfrac{1}{4}\bar{E}/E_d. \qquad (5a)$$

Here σ_d is the displacement cross section for the energy region considered, n is the number of target atoms per unit volume, and N is the number of hard-sphere collisions the primary knock-ons make with other atoms in slowing down to an energy E_s corresponding to the heat of sublimation of the target. If binary collisions are assumed in a random-walk calculation,[12] the total number of atomic layers (including the surface layer) contributing to sputtering is found to be

$$1+N^{\frac{1}{2}}=1+\left[\frac{\log(\bar{E}/E_s)}{\log 2}\right]^{\frac{1}{2}}.$$

By inserting this into Eq. (5a) one gets

$$S=\sigma_d n^{\frac{2}{3}}\left[1+\frac{\log(\bar{E}/E_s)}{\log 2}\right]^{\frac{1}{2}}\times\frac{1}{4}\frac{\bar{E}}{E_d}. \qquad (5b)$$

On the basis of Eq. (5b) Pease calculated values for the sputtering ratio S of silver targets bombarded by protons, deuterons, and helium ions. Curve b in Fig. 2 represents such calculated values for deuterons bombarding silver. (Values are taken from Fig. 1 of Pease's article.) A comparison of curves b, c, and d shows that the values calculated by Pease are considerably larger than the ones calculated by other authors.[4–6] However all three curves predict a decrease of the sputtering ratio with increasing energy.

Contrary to these calculations, Pleshivtsev predicted that the sputtering ratio should increase with increasing energy in the considered energy region $E>E_B$. He tried to correlate the sputtering ratio with the total number of displaced particles, a number which will actually increase with increasing energy. However, as mentioned above, only a fraction of the total number of displaced particles will have a chance to reach the surface and to escape. Pleshivtsev's values of the sputtering ratios are therefore larger than those predicted by other authors. Pleshivtsev's values for the sputtering of copper by deuterons are given in curve a in Fig. 2. The values in curve a are 3 to 4 orders of magnitude higher than those in b, c, and d and they increase with increasing energy.

In conclusion, the experimentally-determined sputtering ratios presented here lie between those calculated by Goldman and Simon[4] and Pease[7] and agree with them within a factor of 2; but they disagree with those reported by Pleshivtsev by 3 to 4 orders of magnitude. The data also show a decrease of the sputtering ratio with increasing ion energy, in qualitative agreement with theoretical predictions[4–7] but contrary to the findings of Pleshivtsev. Therefore on the basis of these results Pleshivtsev's claim that the theory of Goldman and Simon is "incorrect in general" does not seem justified. Furthermore, the present results indicate that the distribution of the sputtered particles deviates from a cosine distribution in the energy range investigated.[13] This makes a definition of the sputtering ratio dependent on the direction of the escaping target atoms.

Further experiments will be conducted with protons, deuterons, and helium ions bombarding copper and silver single crystals at different angles of incidence in the energy range from 100 to 200 kev and 0.8 to 4.0 Mev with the present experimental setup as well as by a mass spectrometric method.

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[12] S. Chandrasekhar, Revs. Modern Phys. **15**, 12 (1943).

[13] For corresponding results for low-energy sputtering, see G.K. Wehner, J. Appl. Phys. **31**, 177 (1960). More references are given in the article.