quantities in Eq. (15) may be shown to be

$$\begin{aligned}|\hat{\theta}\cdot\mathbf{M}_{k\frac{1}{2}}|^2&=R^2\cos^2\theta[(A_k+B_k)^2\cos^2\phi\\&\qquad+(A_k-B_k)^2\sin^2\phi],\\|\hat{\phi}\cdot\mathbf{M}_{k\frac{1}{2}}|^2&=R^2[(A_k+B_k)^2\sin^2\phi\\&\qquad+(A_k-B_k)^2\cos^2\phi],\\|\hat{\theta}\cdot\mathbf{M}_{k,-\frac{1}{2}}|^2&=R^2 4B_k^2\sin^2\theta,\\|\hat{\phi}\cdot\mathbf{M}_{k,-\frac{1}{2}}|^2&=0,\end{aligned}\tag{16}$$

where

$$A_3=-(\sqrt{6})\cos\rho;\quad B_3=\sqrt{2}\sin\rho,$$
$$A_1=-(\sqrt{6})\sin\rho;\quad B_1=-\sqrt{2}\cos\rho,$$

and

$$2R=\langle\alpha\tfrac{1}{2}\|M\|\alpha'\tfrac{3}{2}\rangle.$$

Substituting these results into Eq. (15) and utilizing the definitions of $\cos\rho$ and $\sin\rho$ as given by Eq. (13), one gets

$$\begin{aligned}p_3(\theta,\phi)&=2R[4[(3+\eta^2)/3]^{1/2}\\&\qquad+(3\cos^2\theta-1+\eta\sin^2\theta\cos2\phi)],\\p_1(\theta,\phi)&=2R[4[(3+\eta^2)/3]^{1/2}\\&\qquad-(3\cos^2\theta-1+\eta\sin^2\theta\cos2\phi)].\end{aligned}\tag{17}$$

Arbitrarily factoring out $2R$, the reduced matrix element, Eq. (17) becomes the expression for p_3 and p_1 given by Eq. (8) in the text.

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Secondary-Electron Emission from Molybdenum Due to Positive and Negative Ions of Atmospheric Gases

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Secondary-electron yields from a clean surface of Mo have been measured for H^+, H_2^+, H_3^+, H^-, O^+, O_2^+, O^-, O_2^-, N^+ and N_2^+ in the kinetic energy range 40 eV to 2 keV. These measurements have been made under ultrahigh vacuum of order 10^{-10} Torr. The rate of variation of the electron yield γ with kinetic energy of the incident ion decreases as the ion mass increases, consistently from H^+ to O_2^+. Evidence is presented to show that kinetic emission is much less affected by monolayer coverage of the surface than potential emissions is. For clean surfaces, the negative-ion yields represent most closely the kinetic-emission characteristics of the bombarding particles.

INTRODUCTION

ELECTRON-EMISSION efficiencies of positive ions of the rare gases bombarding a clean metal surface have been reported in an earlier publication from this laboratory.[1] The present measurements using atomic and molecular ions of hydrogen, nitrogen, and oxygen were undertaken to study the potential-energy dependence of the yields at low energies and the mass dependence of yields in the kinetic-emission range of energies. We have attempted to arrive at some qualitative conclusions regarding the effect of adsorbed gases on the target surface and the relative effects of gas coverage on potential and kinetic emission of electrons.

Electron emission due to positive-ion impact for various ion-target systems has been studied extensively. Due to impact of negative ions, electron emission can occur either by the ion releasing its extra electron into vacuum on impact with the surface or by kinetic ejection. Massey[2] suggests that among the reactions leading to the detachment of an electron from a negative ion, the most effective (in the absence of positive ions) is surface collision if the work function of the surface is greater than the electron affinity of the negative ion. In such a case a resonance transition of the extra electron from the negative ion (to an isoenergetic vacant level in the metal) is possible. The electron yields for negative ions were measured for all cases where the ions are stable. For clean surfaces, these yields represent most closely the kinetic-emission characteristics of the bombarding particles. No attempt has been made to estimate the contribution, if any, to the yield, of reflected negative ions or electrons detached from the negative ion and released into vacuum.

APPARATUS

The apparatus used for these measurements has been described in an earlier[1] publication. The background pressure is in the 10^{-10}-Torr range, the lowest so far recorded being 4×10^{-10} Torr. These low pressures have been achieved by continuous pumping for about a month. The operating pressure with source gas flowing and with the beam turned on did not exceed 2×10^{-9} Torr. The target-and-collector assembly has also been

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* Now at General Atomic, A Division of General Dynamics Corporation, San Diego, California.

[1] P. Mahadevan, J. K. Layton, and D. B. Medved, Phys. Rev. **129**, 79 (1963).

[2] H. S. W. Massey, *Negative Ions* (Cambridge University Press, Cambridge, England, 1950), p. 89.

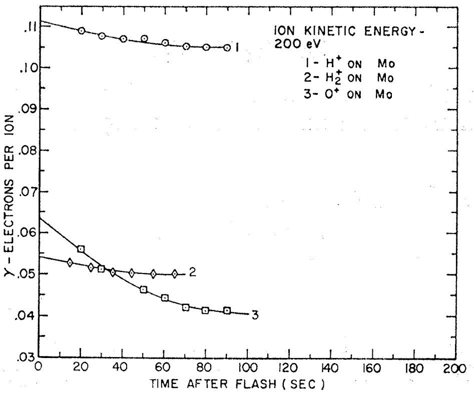

FIG. 1. Variation of secondary electron yield for H^+, H_2^+, and O^+ with time after flash.

described in the same paper. The ion source of conventional design was operated with oxygen, hydrogen and nitrogen of commercial purity. The life of a tungsten filament in oxygen was not more than about 40 h. No attempt was made to lengthen the lifetime of the filament since it was comparatively easy to replace.

The target (Mo ribbon 0.001 in.×1.25 in.×0.5 in.) was cleaned by the flash-filament technique. The procedure was discussed in the earlier paper. After a lengthy preliminary processing, each yield value was taken following a flash for 5 sec at temperatures of order 2000°K. The low-energy data (below 300 eV) have been obtained by running the ion-source output at constant energy and biasing the target suitably.

VARIATION OF THE ELECTRON YIELD WITH TIME AFTER FLASH

The clean-surface values of the electron yields for various positive and negative ions are obtained by extrapolation of curves showing the variation of the yield with time after flashing the target. At low incident-ion energies, the time-variation curves for the positive ions show the characteristic[1] exponential decay until a monolayer is formed on the surface. This behavior is observed for all the positive ions at kinetic energies below about 200 eV. At higher energies the decrease in yield during monolayer coverage due to the potential energy of the ion is more than offset by the strong kinetic-energy dependence of the total electron yield, particularly for the light ions. The effect then, is that the time-variation curve looks like what would be expected for energetic neutral atoms bombarding the surface—a monotonic increase with time. In fact, negative ions bombarding the surface show the same behavior as do neutral atoms since no potential emission is possible for these species.

The percentage change in yield from the clean to a monolayer-covered surface is small for positive hydrogen ions and much larger for positive ions of oxygen and nitrogen. This is qualitatively in agreement with Hagstrum's[3] results of absorption-rate measurements on tungsten. He observed a much larger pressure rise on flashing the target after a given cold interval when N_2 was admitted as an adsorbable impurity than with H_2. Typical time variation curves for H^+, H_2^+, and O^+ ions at 200 eV are shown in Fig. 1. Propst,[4] however, observed the opposite effect with the same adsorbable impurities. We are inclined to conclude that a hydrogen background in the vicinity of a flashed target makes it easier to clean the surface. This is consistent with Moore and Unterwald's[5] finding that molecular hydrogen is readily desorbed from W and Mo at temperatures of order 1000°K. Additional evidence in support of this finding is obtained from Yarwood's[6] recent study of the flash-filament technique for cleaning metal surfaces under ultrahigh vacuum.

At background pressures in the 10^{-10}-Torr range, the time for the formation of an actual monolayer on the surface should be about 15 min assuming the maximum sticking probability of unity for the particles incident on the surface. The time-variation curves, however, show a monolayer formation time of order 2 min only. Thus, even at fractional coverage, the electron yield has decreased to equivalent monolayer values. The extreme surface sensitivity of the mechanism of secondary-electron emission due to low-energy ion bombardment is apparent.

RELATIVE EFFECT OF MONOLAYER COVERAGE OF SURFACE ON POTENTIAL AND KINETIC EMISSION

While measuring[1] the electron yields for Ar^+ and He^+ from Mo, it was observed that an approximately constant difference in yield existed between the clean-surface and monolayer-covered-surface values over the entire energy range. (The monolayer-covered-surface

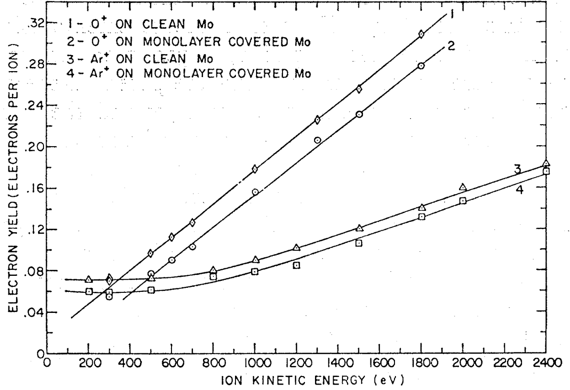

FIG. 2. Electron yields from clean and monolayer-covered surface of Mo bombarded by Ar^+ and O^+.

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[3] H. D. Hagstrum, Phys. Rev. 104, 1516 (1956).

[4] F. M. Propst and E. Lüscher, Phys. Rev. 132, 1037 (1963).

[5] G. E. Moore and F. C. Unterwald, J. Chem. Phys. 40, 2626 (1964).

[6] J. Yarwood and K. J. Close, Vacuum 15, 24 (1965).

yields are obtained from the time-variation plots of γ_i.) A similar feature has been observed for O^+ and O_2^+ ions over a wide energy range. Typical curves showing the kinetic-energy dependence of the electron yields from a clean Mo surface and a monolayer-covered Mo surface bombarded by Ar^+ and O^+ are shown in Fig. 2. Hagstrum[3] obtains the same effect from clean and nitrogen-covered W bombarded by Kr^+ and Xe^+, respectively. Propst[4] has subsequently observed a similar pattern for H_2^+ incident on clean and monolayer-covered tungsten in the limited energy range 50 to 150 eV. For a system like Ar^+ on Mo, where the threshold for kinetic emission of electrons is rather well observed, it is clear that the potential-energy contribution to the total yield is very sensitive to surface contamination. If this contribution be subtracted from the total yield, we get essentially the same curve for both the clean and monolayer-covered surfaces. A noticeable potential-energy contribution is observed for Ar^+, O^+, and O_2^+ up to about 2-keV kinetic energy. Over this energy range, it appears reasonable to conclude that the kinetic-emission contribution is relatively much less dependent on monolayer coverage than the potential-emission factor.[7] This pattern of yield variation is observed within a much smaller range of energies for H^+ and N^+ on Mo (up to about 300 eV). The time variation characteristic of potential emission is not observed for these ions at higher energies.

RESULTS AND DISCUSSION

General Comments

The electron yields from a clean surface of molybdenum bombarded by ions of oxygen, nitrogen, and hydrogen are given in Figs. 3, 4, and 5, respectively. Each value of γ has been obtained by extrapolation of a time-variation plot. The rate of variation of γ with kinetic energy decreases as the mass of the incident positive ion increases, consistently from H^+ to O_2^+. Our earlier data[1] for He^+ and Ar^+ on molybdenum also agree with this pattern.

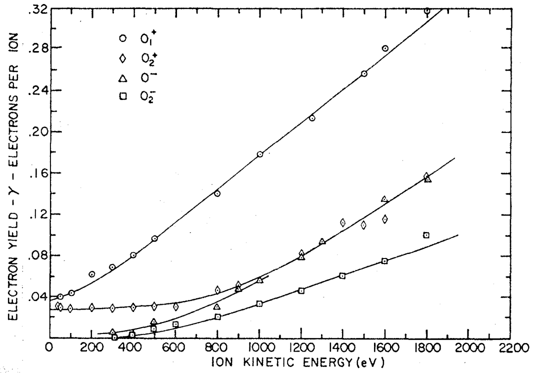

FIG. 3. Electron yields for O^+, O_2^+, O^-, and O_2^- from a clean surface of Mo.

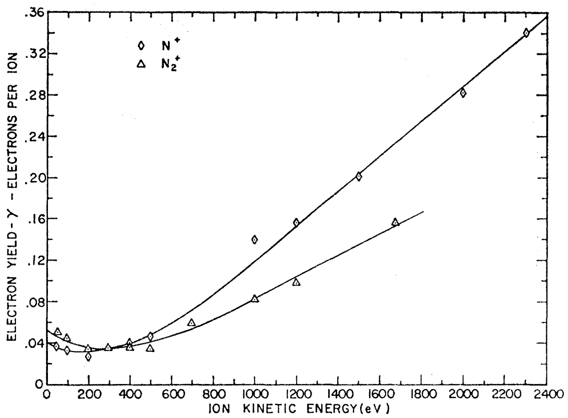

FIG. 4. Electron yields for N^+ and N_2^+ from a clean surface of Mo.

For the molecular ions, at energies below 200 eV where potential emission of electrons is the more predominant process, we observe no clear dependence of the yield on the first ionization potential of the bombarding ion. Since H_2, N_2, and Ar have approximately the same first ionization potentials, it is instructive to compare the electron yields for the three ions bombarding the same target. Comparing with our earlier measurements[1] for Ar^+ on Mo, it is seen that the yield for the atomic ion is much larger than for either of the molecular ions.

In the case of the molecular ions, only a smaller fraction of the available potential energy is obviously used for electron ejection from the metal, due possibly to excitation of vibrational levels of the molecule. This is in agreement with the prediction of Propst and Lüscher.[4] The atomic ions H^+, N^+, and O^+ do not show the same variation with the first ionization potential as the molecular ions. The H^+ ion shows very strong kinetic-energy dependence even at the lower energy limit of our measurements.

Negative-Ion Yields

The few available measurements of negative-charge loss from completely untreated metal surfaces bombarded by negative ions give larger efficiencies of negative-charge loss than due to bombardment by positive ions of the same species and kinetic energy. For primary negative ions, the measured efficiencies could include reflected negative ions as well. We have measured the yields for O^- and O^-_2 from gas-covered and clean surfaces of Mo, and for H^- from a clean surface. The energy dependence of the yields for O^- and O_2^- from a gas-covered Mo surface is shown in Fig. 6. For purposes of comparison, the yields for O^+ and O_2^+ from the same surface are also given in the same figure.

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[7] In support of this conclusion, we observe that the percentage change in yield for 600-eV Ar^+ on Mo, from the first measurement at 15 sec after a flash to a monolayer-covered surface, is about 25%. From our unpublished data, the corresponding change for an Ar neutral beam at 600 eV on Mo is only of order 8%.

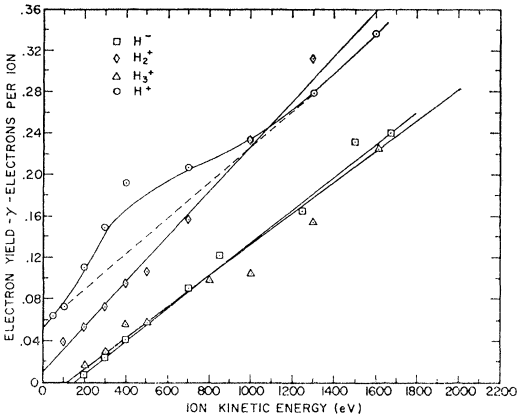

FIG. 5. Electron yields for H^+, H_2^+, H_3^+, and H^- from a clean surface of Mo.

The negative-ion yield exceeds the positive-ion value over the entire energy range. This result is in agreement with Zandberg[8] who used positive and negative ions of Na, Cl, I, and Bi. Perhaps the reason for this apparent anomaly is that the extra electron from the incident negative ion is detached and released into vacuum more efficiently when the work function of the targer metal is lowered by adsorption of impurities like alkali metals. This situation is very likely for negative ions of the halogens in view of their relatively large electron affinities. Mass analysis of the negatively charged particles leaving an untreated metal surface bombarded by positive and negative ions has been made by Ayukhanov *et al.*[9] They find that in some cases, particularly when alkali-metal or alkali-halide impurities are present on the surface, the coefficient of secondary negative-ion emission can be very high. This reference is cited merely to show that a measurement of the total negative-charge loss from an impure surface bombarded by positive or negative ions throws little light on the interaction process.

The clean-surface values of the yield for negative ions are much smaller than for an untreated surface. The variation of the yield with surface coverage shows the characteristics of kinetic emission due to ground-state energetic neutral atoms. A typical time-variation plot for H^- on Mo is given in Fig. 7. The data for O^- and O_2^- on clean Mo are given in Fig. 3 and for H^- in Fig. 5.

Oxygen Ions

The electron yield curve for O_2^+ is almost flat up to 500-eV kinetic energy and then increases rapidly due to onset of a kinetic-energy-dependent mechanism of electron emission. If the invariant component γ_{pot} is subtracted from the total yield for O_2^+, we get a kinetic-emission threshold at about 500-eV energy. However, a finite yield has been measured down to about 150 eV for O_2^- ions. It is reasonable to assume that, below the kinetic-emission threshold of 500 eV, the yield for O_2^- arises from reflection of the primary negative ion without change of charge or detachment of the electron from the negative ion and its release into vacuum. Experimentally, we have at present no means of distinguishing between reflected negative ions and secondary electrons arriving at the collector. It is not possible to estimate a kinetic-emission threshold for O^+ in this way since the yield appears to be strongly dependent on kinetic energy even at 40 eV, the lowest we have used so far. The electron yield for O^+ is larger than that for O_2^+ over the entire energy range investigated here. This is not surprising, considering the facts that the ionization potential of the oxygen atom is greater then that for the molecule, the atomic ion is quite possibly in an excited state, and some energy is possibly absorbed in the vibrational excitation of the molecule. Since the excited states of O^+ are not identifiable by threshold measurements for formation of these ions,[10] the dependence, if any, of the yield on bombarding electron energy in the ion source was not investigated. At higher incident-ion energies Large[11] observes that from tungsten, the yields for O_2^+ are larger than that for O^+.

For O^+ and O_2^+, potential ejection probably occurs by direct Auger neutralization. The two-stage process of resonance neutralization of the ion into a metastably excited state of the atom followed by Auger de-excitation to the ground state of the atom is not very probable, since the energy values of the metastable states for O^+ and O_2^+ are too low to enable an electron of the metal to leave the surface barrier. If V_e is the excitation energy of the atom and ϕ the work function of the metal, the maximum kinetic energy of an electron released from the metal by the two stage process is equal to $(V_e - \phi)$. For the metastable states of O and

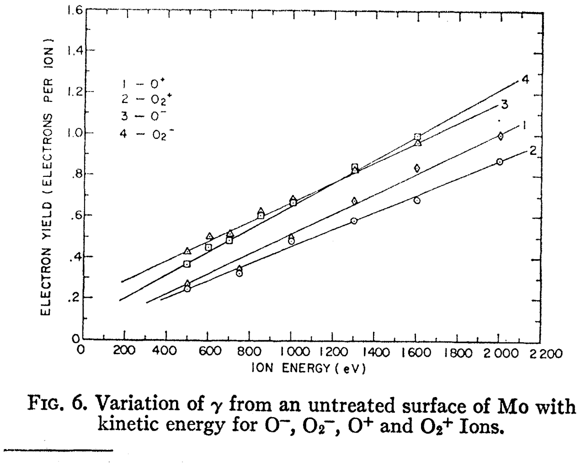

FIG. 6. Variation of γ from an untreated surface of Mo with kinetic energy for O^-, O_2^-, O^+ and O_2^+ Ions.

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[8] E. Ya. Zandberg, Zh. Techn. Fiz. **25**, 1386 (1955).

[9] A. Kh. Ayukhanov *et al.*, U. S. Atomic Energy Commission Translation Series, No. 6089, 1961, p. 158 (unpublished).

[10] D. R. Bates, *Atomic and Molecular Processes* (Academic Press Inc., New York, 1963), p. 435.

[11] L. N. Large, Proc. Phys. Soc. (London) **81**, 1101, 1963.

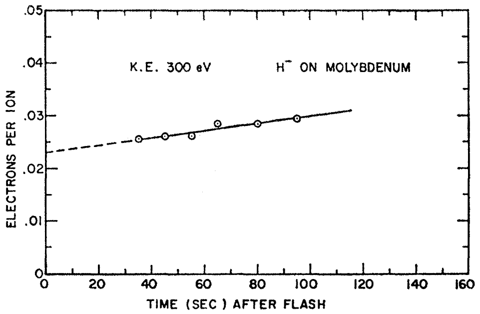

FIG. 7. Variation of γ for H^- with time after flash.

O_2, this will be negative, indicating that no electrons can leave the metal. However, it is possible that Auger de-excitation can take place from the nonmetastable $^5S_0$ state having excitation energy of 9.11 eV which falls just below the Fermi level for Mo.

Hydrogen Ions

The electron yields for all the hydrogen ions (H^+, H_2^+, H_3^+ and H^-) show very strong dependence on kinetic energy. As pointed out before, the rate of variation of the yield with kinetic energy is larger for the hydrogen ions than for the heavier ions. The dependence of the yield on kinetic energy or velocity of the incident ions is different from the results of Dorozhkin and Petrov.[12] Below 2-keV energy, the yield is observed to decrease as the incident mass increases from H_1^+ to H_3^+. However, there appears to be a reversal at the maximum of the energy range when γ is plotted against velocity. Thereafter $\gamma_{H_3^+} > \gamma_{H_2^+} > \gamma_{H^+}$. It is reasonable to conclude that below about 2-keV energy the molecular ions H_2^+ and H_3^+ are not dissociated in flight to be equivalent to two or three energetic particles bombarding the surface with a half or third, respectively, of the original energy. Since the background and operating pressures in Dorozhkin and Petrov's system were 10^{-8} and 10^{-5} Torr, respectively, we suspect that their results correspond to a contaminated surface. Our experimental evidence in support of the above statement is as follows: Using our system we have measured the electron yields for H^+ and H_2^+ bombarding a completely untreated Mo surface at a pressure of order 1.0×10^{-9} Torr. These measurements were taken after overnight pumping and an interval of approximately 15 h from the previous flash. The results are shown in Fig. 8. The yield for H_2^+ is larger than that for H^+, though the ratio $\gamma_{H_2^+}/\gamma_{H^+}$ is much less than 2.

The shape of the yield curve for H^+ between the energies 200 eV and 700 eV in Fig. 5 is not clearly understood, though the data are quite reproducible. If the nonlinear part of the H^+ yield curve is omitted and the low- and high-energy sections of the curve are linked as shown by a dashed line, it is seen that the yield curves for H^- and H^+ are nearly parallel over the entire energy range. The H^- curve then represents the kinetic contribution to the total electron yield. In this case, the negative-ion yield arises from the kinetic energy of the incident particle only.

DEPENDENCE OF THE H_2^+ YIELD ON ENERGY OF THE BOMBARDING ELECTRON IN THE ION SOURCE

The electron yield for H_2^+ at two different beam energies (500 and 150 eV) was measured for various bombarding electron energies in the ion source. The results are shown in Fig. 9. No contribution to the electron yield from the electron excitation of the ion was observed over the range 25 to 60 eV for the ionizing electrons. The H_2^+ ion could be dissociated into normal H and H^+ at an onset potential of 18 V. The dissociation increases considerably at an onset potential of 28 V when H_2^+ is excited to a repulsive state. Electron excitation leading to dissociation of the H_2^+ ion would not obviously affect the yield for the molecular ion. The relative abundance of H_1^+, H_2^+, and H_3^+ emerging from the ion source as a function of source pressure or bombarding electron energy could not be measured with any degree of reliability.

POSSIBLE MODE OF FORMATION OF H_3^+

Saporoschenko[13] contends that the most probable mode for the formation of the H_3^+ ion is the proton-transfer reaction

$$H_2^+(\text{slow})+H_2(\text{slow}) \rightarrow H_3^+ + H + \Delta E.$$

The formation of the ion therefore depends on the concentration of H_2^+ and H_2 in the source. There is qualitative support for this view from our observation that the source pressure has to be increased considerably beyond the setting for the production of H_2^+ to get a reasonably large H_3^+ ion beam.

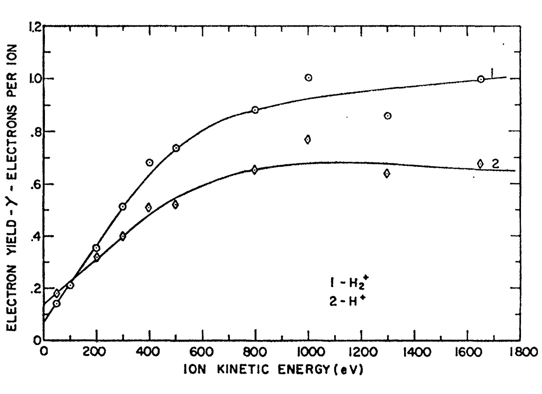

FIG. 8. Electron-yield variation with kinetic energy for H^+ and H_2^+ from gas-covered surface of Mo.

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[12] A. A. Dorozhkin and N. N. Petrov, Zh. Techn. Fiz. **33**, 350 (1963) [English transl.: Soviet Phys.—Tech. Phys. **8**, 257 (1963)].

[13] M. Saporoschenko, J. Chem. Phys. **42**, 2760 (1965).

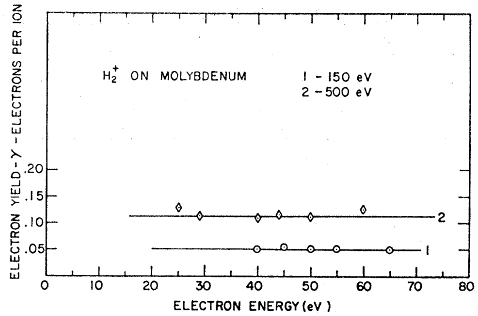

FIG. 9. Dependence of the electron yield for H_2^+ on Mo on energy of bombarding electrons in the source.

Nitrogen Ions

At very low energies, where potential emission is predominant, the yield for N_2^+ is greater than that for N^+. This is consistent with the higher value of the ionization potential for N_2. The yields for N_2^+ and N^+ decrease as kinetic energy of the ions increases up to about 400 eV, and then increase rapidly with beam energy. The rapid change in slope of the yield curves at about 400-eV energy indicates the onset of kinetic emission. In the energy range for kinetic emission, the atomic-ion yield exceeds that for the molecular ion. As in the case of the molecular ions of hydrogen there is no evidence for the dissociation of N_2^+ into two atomic particles each having half the energy. We disagree with Petrov's[14] conclusion that $\gamma(N_2^+)$ at an energy E is equal to $2\gamma(N^+)$ at an energy $\frac{1}{2}E$.

VELOCITY DEPENDENCE OF THE YIELDS

The energy range investigated here is too limited to draw firm conclusions about the velocity dependence of the electron yields. Above a certain velocity threshold, it could be said that the yields are proportional to the incident ion mass. The crossover occurs for H^+, H_2^+, H_3^+ at a velocity of about 3×10^7 cm/sec; for N^+ and N_2^+ at 0.7×10^7 cm/sec and for O^+ and O_2^+ at 1.0×10^7 cm/sec. Our earlier data for Ar^+ ions also appears to fit into this pattern of mass dependence.

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[14] N. N. Petrov and A. A. Dorozhkin, Fiz. Tverd. Tela **3**, 53 (1961) [English transl.: Soviet Phys.—Solid State **3**, 38 (1961)].

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Localized Magnetic Moments in Dilute Metallic Alloys: Correlation Effects[*]

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We discuss qualitatively the importance of the correlation energy in determining the ground state of a metal with an impurity atom. For a single, partly occupied impurity d-state orbital, the correlation energy acts to prevent the appearance of a nonvanishing ground-state spin, so that this simple nondegenerate model actually has a complicated structure. In *one* dimension, we show that this model of an impurity can never lead to a localized moment. In *three* dimensions, if we take linear combinations of Bloch functions transforming according to the irreducible representations of the point group of the impurity+crystal, we find that most of the new wave functions are entirely decoupled from the impurity, and only a small subset interacts with it. The noninteracting majority of states determine the Fermi level, which we therefore take to be fixed. The ground state of the band states interacting with the impurity states depends on the two-body Coulomb repulsion U, and we find that for sufficiently small U the ground state has an even number of electrons with total spin $S=0$. As U is increased above a certain critical value, the ground state of the interacting subsystem changes to an odd number of electrons, having total spin $S=\frac{1}{2}$, and a localized moment is said to exist. The introduction of orbital degeneracy for the impurity d state, and of Hund's rule matrix elements, makes the localized moment much stabler. The results are obtained by a combination of exact energy-level ordering theorems and a Green's-function calculation in the t-matrix approximation.

I. INTRODUCTION AND THEOREMS

THE conditions under which a localized magnetic moment is associated with a solute atom in a dilute alloy have been investigated within the framework of the Hartree-Fock (HF) approximation.[1–3] It is well known that in metals the HF approximation overestimates the strength of the effective exchange interaction through the neglect of correlations between electrons of opposite spin orientations (i.e., the "correlation hole"). As a result, the HF theory of ferromagnetism

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[*] Part of this work is a contribution of the Laboratory for Research on the Structure of Matter, University of Pennsylvania, covering research sponsored by the Advanced Research Projects Agency.

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[1] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).

[2] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[3] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).