A shift in the absorption limit with charge-carrier density should also be observable at sufficiently high charge-carrier densities in other semiconductors. However, the absorption by free charge carriers at the high densities needed would, in general, mask the intrinsic absorption limit and thereby prevent the effect from being observed.

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Origin of the Emission of the Oxygen Green Line in the Airglow[*]

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IT is well known that the airglow emission of the oxygen green line at λ5577A cannot be attributed to the ordinary chemical sources if the altitude of the airglow layer is greater than that of the E layer. Furthermore, ionic recombinations involving negative ions in Region F are not sufficient to lead to an airglow emission. Finally, while the hypothesis of incoming particles exciting this emission has been put forward, it remains vague and cannot account for the variations which are observed.

According to the observational data,[1] the height of the emission layer is of the order of 250±50 km, and the maximum of intensity occurs at local midnight ±2.5 hours. The observed annual variation shows several maxima and indicates, therefore, a quite complex variation. Finally, the isophotal plots of the intensity changes of various parts of the sky suggest the presence of a definitive emission pattern in the high atmosphere.

In order to explain such an emission, recourse must be made to results obtained by Nicolet and Mange[2] on the vertical distribution of molecular oxygen. The charge-exchange process considered by Bates and Massey[3] can be applied in the following form in the F_2 layer:

$$O^+ + O_2 \rightarrow O + O_2^+. \tag{1}$$

The reaction (1) is followed by

$$O_2^+ + e \rightarrow O' + O'', \tag{2}$$

namely, a dissociative recombination process first discussed by Bates and Massey[3] and calculated by Bates.[4] Dissociative recombination of O_2^+ is a powerful excitation mechanism for the green line in the airglow.

Because molecular and atomic oxygen are in diffusive equilibrium at 200 km, we can assume the following vertical distributions:

$$n(O) = n_0(O) \exp[-(1+\beta)\zeta], \tag{3}$$

and

$$n(O_2) = n_0(O_2) \exp[-(2+\beta)\zeta], \tag{4}$$

in which $n_0(O)$ and $n_0(O_2)$ denote the concentrations at the reduced[5] height $\zeta = 0$, $n(O)$ and $n(O_2)$ are the concentrations at height ζ, and β is the scale height gradient of atomic oxygen.

Numerical values[2] show that O_2 is still an important constituent in Region F; of the order of 5×10^7 cm^{-3} at 200 km, 5×10^6 at 250 km, 5×10^5 at 300 km and 10^5 at 350 km. According to ionospheric observations,[6] an average peak of the night-time F_2 layer may be considered at heights of the order of 300–350 km. The vertical distribution of the electron concentration n_e can be represented[5] by the following formula:

$$n_e = (n_e)_0 \exp\{\tfrac{1}{2}(1+\beta)[1-\zeta(1-\eta)-e^{-\zeta}]\}, \tag{5}$$

in which η denotes a parameter giving the form of the particular distribution. If $\eta = 0$, the conventional form is obtained in which the total electron content of the layer is three times the content below the peak. If $\eta = 1/(1+\beta)$, the recombination coefficient can be proportional to the pressure and the total electron content is six times the content below the peak. It is known that these extreme forms may represent the behavior of the F_2 layer[7] in winter and summer.

Ionization potentials of O and O_2 being 13.60 ev[8] and 12.04 ev,[9] respectively, O_2^+ obtained by (1) is in the electronic state $(^2\Pi_g)$ from $v=0$ to $v=6$ at most. The dissociation potential of oxygen being 5.11 ev,[10] process (2) *a priori* leads to three possibilities as far as the energy balance is concerned:

$$O_2^+ + e \rightarrow 2O(^1S), \text{ or } O(^1S)+O(^1D), \text{ or } O(^1S)+O(^3P).$$

From this, one concludes that the emission of the green line might be produced by this means. If the complete use of the energy may yield two excited atoms ^1S, it must be pointed out that the rate of the emission processes depends on the repulsion curves of states leading to dissociation products ^1S, ^1D, and ^3P.

At F_2 layer heights, $n(O^+) > n(O_2^+)$, so that, thanks to (3), (4), and (5), we may deduce the following vertical distribution of the green line emission:

$$I_{5577} \propto \exp\left\{(1+\beta)\left[1-\zeta\left(\frac{2\beta+3}{1+\beta}-\eta\right)-e^{-\zeta}\right]\right\}. \tag{6}$$

The gradient of the scale height being $\beta = 0.3$, the peak of the emission corresponds to a value of ζ varying from -1 to -2 below the peak of the electron concentration (300–350 km), i.e., an altitude of 250 km.

It follows from these calculations that an airglow emission in Region F is possible. A complete account of this work will be published elsewhere. This will show the interdependence of the emission of the green line and of the properties of an ionospheric layer in which molecular oxygen ions play an important part on account of vertical transport by diffusion.[11]

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Threshold Energies for Sputtering and the Sound Velocity in Metals

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THE author has recently[1] described experiments which show that the minimum threshold energy for sputtering is a function of the angle of incidence of the bombarding ions. Previous attempts to measure threshold energies failed to give reliable results because they were made either in the glow discharge or with wires which are small compared to the ion sheath thickness;[2,3] in both cases, however, the angle of incidence is undetermined.

With a low gas pressure (1 micron) and a large sputtering electrode immersed in a plasma of high density ($10^{11}-10^{12}$ per cm^3), it is possible to avoid collisions of the ions within the ion sheath and to approach the plane case with predominantly

TABLE I. $\Delta H_v(298)$ = Heat of vaporization[a] at 298°K [ev]. E = Modulus of elasticity[b] [kg/mm^2]. μ = Poisson constant.[b] $v_s=[E(1-\mu)/\mu(1-\mu-2\mu^2)]^{\frac{1}{2}}$ = bulk sound velocity in 10^5 cm/sec. V_0^*(Hg) = Threshold energy for sputtering by Hg ions under normal incidence [ev], corrected for neutralization energy and work function. $M=2(2em_gV_0^*)^{\frac{1}{2}}m_m/(m_g+m_m)$ = momentum transferred at V_0^* [ev-sec/cm].

	$\Delta H_v(298)$	E	μ	v_s	V_0^*(Hg)	$M\times v_s$
Al	3.26	7220	0.34	6.45	120–140	34 – 36.6
Si	3.91	11 500	0.42	11.2	60– 70	43 – 46.4
Ti	4.92	10 500	0.36	6.35	110–130	51.6– 56
V	5.2	15 000	0.35	6.24	120–130	56.2– 58.4
Cr	3.68	19 000	0.31	6.15	60– 80	37.6– 45.6
Fe	4.2	21 550	0.29	6.1	60– 70	41.6– 44.8
Co	4.56	20 380	0.31	5.6	80–100	46 – 51.4
Ni	4.41	19 700	0.32	5.6	70– 90	42.4– 48.4
Cu	3.56	12 500	0.35	4.7	50– 70	32.2– 36
Ge	3.4	8000	0.32	4.6	40– 50	31.2– 34.8
Zr	5.43	6970	0.37	4.33	120–130	60.4– 62.4
Cb	7.6	16 000	0.35	5.5	120–130	77.4– 80
Mo	6.75	33 630	0.31	6.7	80–100	78.4– 87.4
Rh	6.0	38 640	0.26	6.15	70– 80	70.8– 75.6
Pd	4.05	12 360	0.39	4.5	50– 80	44.6– 56.4
Ag	3.04	8160	0.37	3.68	40– 50	32.8– 36.6
Sb	2.74	5600	0.33	4.3	30– 40	36 – 41.2
Hf	7.4	8500	0.37	3.34	150–180	76.8– 83.6
Ta	8.7	18 820	0.35	4.25	120–140	89 – 96.6
W	8.75	41 520	0.30	5.36	80–100	92.8–104
Re	8.21	53 000	0.26	5.65	70– 80	91.4– 98
Pt	5.86	17 320	0.39	3.98	70– 90	66 – 75.2
Au	3.94	7900	0.42	3.22	40– 50	40.8– 45.6
Pb	2.02	1600	0.44	2.17	20– 40	20 – 28.2
Th	6.5	7970	0.26	2.89	120–140	68.6– 74
U	5.43	13 380	0.30	3.08	70– 80	56 – 60
B	3.91	—	—	(13.1–14.7)	200–250	(42.8)
C	7.45	—	—	(14.7–16)	500–600?	(82)?

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perpendicular impacts. The study of deposits, sputtered under these conditions, shows that a well-defined minimum ion energy (V_0^*) is characteristic for every gas-metal combination.

V_0^*(Hg), (normal incidence of Hg ions) was measured for 26 metals (Table I). These threshold energies cannot be brought into agreement with existing threshold theories.[2,4] It turns out, however, that they follow (so far without exception) a simple law: The product of the momentum transferred at V_0^* from the ion to the metal atom (central collision between free elastic spheres), with the bulk sound velocity of the metal, is proportional (factor ≈11.2) to the heat of sublimation (Fig. 1); hence, threshold energies can be calculated from

$$V_0^*=\left(\frac{1.68\times10^5(m_g+m_m)\phi}{m_g^{\frac{1}{2}}v_sm_m}\right)^2,$$

where V_0^* is in ev; m_g = atomic weight of ion; m_m = atomic weight of metal; v_s = bulk sound velocity of metal in cm/sec; and ϕ = heat of sublimation of metal in kcal/mol. Part of V_0^* is supplied by the neutralization energy V_i and part is used for overcoming the work function W of the material; hence, $V_0^*=V_0+V_i-W$, where V_0 is identical with the measured voltage difference between sputtering electrode and plasma. A correction of v_s for temperature (200–300°C) is small enough in most cases to stay within the experimental error and is omitted.

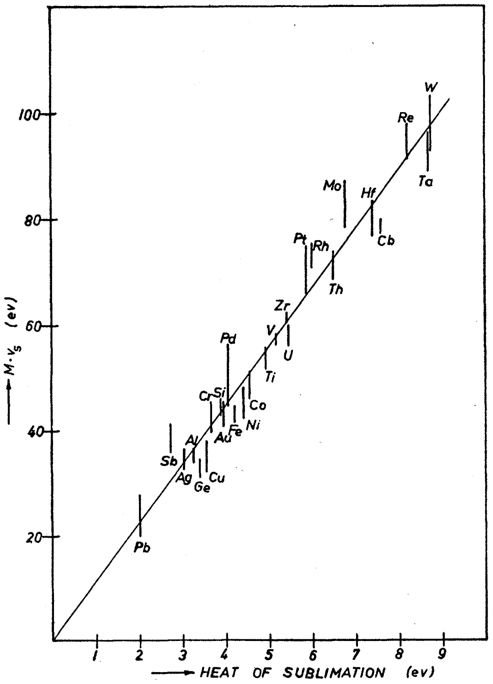

FIG. 1. Product of transferred momentum and bulk sound velocity *versus* heat of sublimation.

This law is in good agreement with other experimental results, such as those for Pt in Xe,[5] and those from recent work of Bradley[6] concerning alkali metals in inert gases. Hence, there is reason to believe that this law is of a general nature and is applicable to all gas-metal combinations, as long as "physical" and not "chemical" sputtering (e.g., C in H_2) takes place.

The bulk sound velocity of boron, not listed in the literature, would hereby be determined to be 14×10^5 cm/sec (between Si and diamond). Measurements with C (graphite) seem to indicate that it is the maximal sound velocity which determines the threshold energy. Unfortunately, sufficient data concerning $v_{s\,\max}$ from measurements in metal single crystals are not available in the literature for the introduction of this additional correction.

The significance of the sound velocity here, although not yet fully understood, is obviously to introduce the elastic constants of the material, which determine what part of the transferred energy with the momentum directed to the inside of the material arrives at the surface with a momentum reversed in direction. This part has to be at least equal to the binding energy of a surface atom before sputtering ensues.

A more detailed paper will be submitted later.

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Infrared Absorption of NiO

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THE Verneuil method[1] (or flame-fusion method) of growing crystals is well known and has been utilized for some time in producing crystals of sapphire, rutile, etc. Recently this method has been used at this laboratory to produce single crystals of NiO. These crystals are dark green to black in color and are easily cleaved. Their crystal structure is face-centered cubic with a lattice spacing of 4.17A which agrees with previously published data.[2] The melting point, as determined during the actual growth, is slightly above 1900°C.

The over-all resistivity at room temperature of these crystals, as measured by a megohm bridge, is 7.0×10^6 ohm cm, this value being somewhat less than the 10^8 ohm cm usually reported in the literature for NiO in the polycrystalline form.[3]

A $1\times5\times10$ mm plate was cleaved from the NiO single-crystal boule; infrared transmission in the wavelength range of 1μ to 15μ was observed with this specimen using a Perkin Elmer Model-112