

intensity with wave-length, with power and with aerial directivity all seem to confirm this, for these are the factors which determine the intensity of a received scatter signal itself.

It is generally assumed that ionosphere storms of the kind mentioned are caused by corpuscles ejected from the sun, the effect of which, while it is pronounced in the case of the *F* layer, is small or even negligible at the height of the *E* layer. If the 'rumble' is indeed produced in the way suggested, it would seem that the corpuscles do produce a marked effect upon the *E* layer, at least upon the ionic clouds, if not upon the regular structure of the ionization. As to the exact form this effect may take, it would be rash to attempt an explanation, but it is suggested that the clouds are affected in such a way that a kind of Doppler effect is imparted to the scattered energy. A further point is that the above postulation as to the cause of the 'rumble' would provide additional confirmation of the evidence of Eckersley, Millington and Cox that the scatter is indeed from a point in the atmosphere and not from a distant point on the ground.

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- ¹ Eckersley, T. L., *Nature*, 143, 33 (1939).
- ² Eckersley, T. L., *J. Inst. Elect. Eng.*, 86, 658 (1940).
- ³ Eckersley, T. L., Millington, G., and Cox, J. W., *Nature*, 153, 341 (1944).

Shape of Collision-Broadened Spectral Lines

Van Vleck and Weisskopf¹, in an interesting paper, have shown that the well-known Lorentz formula for the shape of a spectral line is incorrect except at frequencies close to the resonance frequency. Since this formula has been considered to be correct for a great number of years, it may be of interest to record that, using a different method, I had reached the same conclusions² as Van Vleck and Weisskopf. This method, although originally developed for the case of a rigid dipole oscillating about an equilibrium position, can easily be adapted to harmonic oscillators.

Consider an assembly of *N* equal harmonic oscillators of which the proper frequency, mass, charge and displacement are denoted by $\omega_0/2\pi$, *M*, *e*, *x*, respectively. In an external field *F*, *x* satisfies

$$\ddot{x} = -\omega_0^2 x + eF/M, \dots (1)$$

whereas the energy is given by

$$E = E_0 - eFx, \text{ where } E_0 = \frac{M}{2} \dot{x}^2 + \frac{M}{2} \omega_0^2 x^2 \dots (2)$$

In a constant field $F = F_0$, the distribution function $f(x, \dot{x})$ (that is, number of oscillators per unit range of *x* and \dot{x}) is proportional to $\exp. -E_0/kT$. For sufficiently weak fields, $f = f_0 + f_1$, where

$$f_0 = C \exp. (-E_0/kT), \dots \int_{-\infty}^{\infty} f_0 dx d\dot{x} = N,$$

and

$$f_1 = C \exp. (-E_0/kT) \frac{eF_0 x}{kT} = -\frac{eF_0}{M\omega_0^2} \frac{\partial f_0}{\partial x}, \quad |f_1| \ll f_0. \quad (3)$$

The polarization is thus given by

$$P_0 = e \int x f dx d\dot{x} = e \int x f_1 dx d\dot{x} = -\frac{e^2 F_0}{M\omega_0^2} \int x \frac{\partial f_0}{\partial x} dx d\dot{x} = \frac{e^2 N F_0}{M\omega_0^2} \dots (4)$$

Consider now a periodic field $F = F_0 \exp. i\omega t$. If instantaneous equilibrium could be reached, the distribution function would be

$$f_{\text{equ.}} = f_0 + f_1 \exp. i\omega t. \dots (5)$$

Assume the actual distribution function to be

$$f = f_0 + f_2 \exp. i\omega t, \dots |f_2| \ll f_0 \dots (6)$$

At any instant of time the oscillators will then tend to reach $f_{\text{equ.}}$ If they are in interaction (collisions) with a medium which is in thermal equilibrium. The main assumption of the present calculation is to suppose that the rate of change of *f* due to these collisions is given by $-(f - f_{\text{equ.}})/\tau$, where the time of relaxation τ may depend on temperature but is independent of *x* and \dot{x} . Adding the rate of change due to oscillation, we find

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial x} \dot{x} + \frac{\partial f}{\partial \dot{x}} \ddot{x} - \frac{1}{\tau} (f - f_{\text{equ.}}); \dots (7)$$

or making use of (1), (5) and (6)

$$\frac{\partial f}{\partial t} = \frac{\partial f}{\partial x} \dot{x} - \omega_0^2 \frac{\partial f}{\partial \dot{x}} x + \frac{eF_0}{M} \frac{\partial f}{\partial \dot{x}} \exp. i\omega t - \frac{1}{\tau} (f_2 - f_1) \exp. i\omega t. \dots (8)$$

Now insert (6) and (3) in (8), neglect terms in $F_0 f_2$ which are small of the second order, and notice that $\partial f_0 / \partial t = 0$. Then

$$\left(i\omega + \frac{1}{\tau}\right) f_2 = \frac{\partial f_2}{\partial x} \dot{x} - \frac{\partial f_2}{\partial \dot{x}} \omega_0^2 x + \frac{eF_0}{M} \frac{\partial f_0}{\partial \dot{x}} - \frac{eF_0}{\tau M \omega_0^2} \frac{\partial f_0}{\partial x} \dots (9)$$

This equation can be solved by putting

$$f_2 = a \frac{\partial f_0}{\partial x} + b \frac{\partial f_0}{\partial \dot{x}}, \dots (10)$$

where

$$a = -\frac{eF_0}{M\omega_0^2} \frac{1}{2} \left\{ \frac{1 + i\omega_0\tau}{1 + i(\omega + \omega_0)\tau} + \frac{1 - i\omega_0\tau}{1 + i(\omega - \omega_0)\tau} \right\},$$

$$b = \frac{\tau}{1 + i\omega\tau} \left(a\omega_0^2 + \frac{eF_0}{M} \right) \dots (11)$$

The total polarization *P* is thus given by (if we note that $\int x \frac{\partial f_0}{\partial x} = 0$, and make use of (11) and (4))

$$P = e \int x f dx d\dot{x} = e \int x f_2 \exp. (i\omega t) dx d\dot{x} = ea \exp. i\omega t \int x \frac{\partial f_0}{\partial x} dx d\dot{x} = \frac{1}{2} \left\{ \frac{1 + i\omega_0\tau}{1 + i(\omega + \omega_0)\tau} + \frac{1 - i\omega_0\tau}{1 + i(\omega - \omega_0)\tau} \right\} P_0 \exp. i\omega t, \dots (12)$$

in agreement with Van Vleck and Weisskopf's equations (17) (18), which are obtained as the real and imaginary parts (the latter multiplied by ω) of *P*/*F*.

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Jan. 10.

- ¹ Van Vleck and Weisskopf, *Rev. Mod. Phys.*, 17, 227 (1945).
- ² Addendum to Report L/T. 157 and Report L/T. 163 of the British Electrical and Allied Industries Research Association.

'Impregnation' of Defect Lattices in Iron Oxide Scales

In the course of an X-ray examination on scales formed on steels, a structure phenomenon was observed which is believed to be of general interest. Magnesia is known to possess a considerably smaller lattice-parameter than ferrous oxide, with which it is isomorphous. If, therefore, wüstite (the FeO solid solution) dissolves magnesium oxide, its parameter would be expected to decrease, as the smaller Mg⁺⁺ ion replaces Fe⁺⁺. To test this, a FeO-MgO solid solution was allowed to form, by coating Arco iron with pure magnesia, and oxidizing in air at 1,000° C.; the scale was then examined by powder-photographs. The result was that the ferrous oxide had split into two phases, both of the same structure (rocksalt type), and, surprisingly, not of a decreased but an *increased* lattice parameter, compared with the oxide formed on non-coated iron under otherwise identical conditions. The accompanying photographs illustrate the effect. The measured dimensions were as follows:

Ferrous oxide phase formed on:	Lattice parameter (A.)
Uncoated iron	4.284
MgO-coated iron	(a) 4.298 (b) 4.317
Pure MgO	4.230

The reason for this expansion is that the magnesium ions, instead of replacing ferrous ions in the wüstite lattice, occupy vacant lattice-positions, until all 'holes' are filled. Thenceforward a normal contraction takes place. The theoretical saturation parameter, derived by extrapolating the known pure wüstite values to the equiatomic composition (FeO), and allowing for the difference in the ionic radii of Fe⁺⁺ and Mg⁺⁺, is 4.328 Å., assuming all vacant sites in single-phase wüstite to be occupied. This would mean an expansion of the cube edge of 4.328-4.284 = 0.044 Å., compared with uncoated iron. The actual expansion, being divided between two phases of practically equal amounts, is $\frac{1}{2} [(4.298 - 4.284) + (4.317 - 4.284)] = 0.023$ Å., that is, in the present case occupation has proceeded to approximately half the saturation value.

Thus it can be said that the defect lattice of wüstite has been 'impregnated' by magnesium ions. Since vacant metallic lattice sites are liable to aid outward diffusion of anions (FeO in scales affords poor protection against further oxidation), the question arises whether by such impregnation the corrosion resistance can be improved. According to Wagner¹, the deficiency of metal ions in oxide structures (for example, Cu₂O, FeO) increases the electrical conductivity and also explains the greater oxidizability of iron compared with other metals (compare, for example, Pfell's work²). This is reflected by the considerable decrease in Fe : O ratio of the ferrous oxide phase, below the value of the stoichiometrical composition, from the iron/scale to the scale/oxygen interface, reported, for example, by the writer³.

Quantitative hot oxidation tests in pure iron, with and without magnesium oxide covering, carried out to detect any protective effect due to the impregnation, have so far shown no improvement of cor-