The expression obtained can be used for the conversion of the measured spectrum into the true radiation spectrum.

Let us consider some special cases of Eqs. (2) and (3).

1. The exciting radiation is weakly scattered and is attenuated according to the exponential law. X-rays approximately satisfy this condition. In this case $L = R$; $R \approx 0$ and formulae (2) and (3) are transformed respectively into

$$I_1 = \frac{1}{2} CkB \frac{1+R_l}{1-R_l^2 e^{-2L_l x_0}} \left[\frac{e^{-kx_0} - e^{-L_l x_0}}{L_l - k} + R_l \frac{e^{-(2L_l - k)x_0} - e^{-L_l x_0}}{L_l + k} \right], \tag{6}$$

$$I_2 = \frac{1}{2} CkB \frac{1+R_l}{1-R_l^2 e^{-2L_l x_0}} \left[\frac{1 - e^{-(L_l + k)x_0}}{L_l + k} - R_l \frac{e^{-(L_l + k)x_0} - e^{-2L_l x_0}}{L_l - k}. \right] \tag{7}$$

2. The exciting radiation is weakly scattered and penetrates to a small depth (for instance, α-particles). Therefore, $L = k >> L_l$; $R \approx 0$ and we obtain:

$$I_1 = \frac{1}{2} CB \frac{(1-R_l^2)\, e^{-L_l x_0}}{1-R_l^2 e^{-2L_l x_0}}, \tag{8}$$

$$I_2 = \frac{1}{2} CB \frac{(1+R_l)\,(1-R_l e^{-2L_l x_0})}{1-R_l^2 e^{-2L_l x_0}},$$

When $x_0 = \infty$

$$I_2 = {}^1\!/_2 CB\,(1+R_l), \tag{9}$$

i.e., with the increase of the size of the grain (d), the coefficient of reflection R_l decreases and, consequently, I_2 decreases.

3. The exciting radiation is weakly scattered and weakly absorbed (gamma rays). In this case the layer is found to be uniformly excited for sufficiently great thicknesses, and, therefore,

$$I_1 = I_2 = \frac{CkB}{2L_l} \frac{1+R_l}{1-R_l^2 e^{-2L_l x_0}} [1 - e^{-2L_l x_0} + R_l (e^{-2L_l x_0} - e^{-L_l x_0})].$$

For an infinitely thick layer, $I_1 = 0$ and $I_2 = {}^1\!/_2 CkB \times (1-R_l)/k_l$, i.e., with the increase of d, the coefficient of reflection decreases and I_2 increases.

In such a way the different nature of the attenuation of the excitation flux leads to the result that an increase of the crushing of the powder of the luminophor increases the brightness of the luminescence in one case and decreases it in the second. Therefore we can imagine a case in which the brightness of the luminescence depends weakly on the degree of dispersion.

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* The formulas obtained are indeterminate if the light of the luminescence is not absorbed. In this case it is necessary during the calculation to use the formulas $t(x) = 1/(1+s_l x)$ and $r(x) = s_l x/(1+s_l x)$ (see reference 3). As a result, expressions are obtained which coincide with the formulas for the intensity of luminescence, given in reference 1.

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29

Concerning Some Thermodynamic Inequalities

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1. IN the thermodynamic investigation of the properties of materials which possess magnetic and dielectric properties that obey the general law set forth, for example, in reference 1, it is possible to obtain thermodynamic inequalities which are the necessary conditions for thermodynamic equilibrium . The present communication is devoted to a brief derivation of such inequalities, and to the obtaining, with the help of the latter, of certain conclusions as to the form of the equilibrium curve of the magnetization of a magnet.

Assuming that each element of the volume of a body is in a state of thermodynamic equilibrium, we can represent the first law of thermodynamics, for media of interest to us, in the following form

$$\Delta e = T\Delta s + (\mathbf{H}\Delta\mathbf{B} + \mathbf{E}\Delta\mathbf{D})/4\pi. \tag{1.1}$$

Following Landau and Lifshitz[1], it is easy to calculate the minimum work done on a body, located in some medium, by external, thermally isolated bodies. In such a case, the energy of the closed system (body + surroundings), when the body is not in equilibrium with the medium, differs from its own maximum value by an amount

$$\Delta S_p = -\frac{R_{\min}}{T_0} = -\frac{1}{T_0}\left[\Delta E - T_0\Delta S - \frac{1}{4\pi} \times \int dV\,(\mathbf{H}\cdot\Delta\mathbf{B} + \mathbf{E}\cdot\Delta\mathbf{D})\right], \qquad (1.2)$$

where ΔE, etc., represent the differences between the equilibrium values of the appropriate quantities and their values in the state of total equilibrium.* It follows from Eq. (1.2) that for the element of volume of a body found in thermodynamic equilibrium with the remaining parts of the body (which can be considered as the medium) the following condition must hold

$$\Delta e - T\Delta s - (\mathbf{H}\cdot\Delta\mathbf{B} + \mathbf{E}\cdot\Delta\mathbf{D})/4\pi > 0. \qquad (1.3)$$

For simplicity, we assume below that $\Delta\mathbf{D} \equiv 0$, and limit ourselves to taking only the magnetic field into account. It is evident that for an electric field, entirely analogous results will follow. Expanding Δe in a power series in Δs and ΔB, we get from Eq. (1.3):

$$\frac{\partial^2 e}{\partial s^2}(\Delta s)^2 + \sum_{i,j}\frac{\partial^2 e}{\partial B_i\partial B_j}\Delta B_i\Delta B_j > 0. \qquad (1.4)$$

The condition of the positive nature of the principal minors of the quadratic form (1.4) gives the corresponding thermodynamic inequality. In this case, in particular, we get

$$(\partial H_i/\partial B_i)_T > 0. \qquad (1.5)$$

We have neglected any change in the number of particles per unit volume. Account of such changes leads to the result that in differentiation in (1.5) must be carried out at constant chemical potential*.

The inequality (1.5) is the analogue of the thermodynamic inequality $(\partial p/\partial V)_T < 0$ and corresponds to the fact that, at constant temperature, an increase in the magnetic induction is always accompanied by an increase in the magnetic field. Thus, in the state of thermodynamic equilibrium, the magnetization curve of a magnet has neither maxima nor minima. For a linear medium ($\mathbf{B} = \mu\mathbf{H}$) it follows from Eq. (1.5) that μ must be greater than zero. We note that for thermodynamic stability of the equilibrium state, it is also necessary that the coefficients of the expansion of Δe in powers of Δs and ΔB_i should be bounded, since in the opposite case, small changes in the parameters would lead to arbitrarilly large changes in the state. Then, from the condition of the finiteness of $(\partial H_i/\partial B_i)_T$, and from the condition (1.5), it follows that as $H \to 0$, the magnetic induction tends toward the value $B(H = 0)$, as the first power of H.

Finally, we note that it follows from the condition (1.5) that for an isotropic magnet, the magnetic field, equal in this case to $\mathbf{H} = (4\pi\mathbf{B}/B)\,(\partial e/\partial B)_s$, and the induction must be parallel*. Actually, in this case the inequality (1.5) takes the following form

$$\frac{1}{4\pi}\frac{\partial H_z}{\partial B_z} = \frac{\partial}{\partial B_z}\left(\frac{B_z}{B}\frac{\partial e}{\partial B}\right) \qquad (1.6)$$

$$= \frac{\partial^2 e}{\partial B^2}\frac{B_z^2}{B^2} + \frac{1}{B}\frac{\partial e}{\partial B} - \frac{B_z^2}{B^3}\frac{\partial e}{\partial B} > 0$$

and for $B_z = 0$ gives the result indicated.

2. We now consider the somewhat more complicated case of a system for whose phenomenological description it is generally not possible to introduce B or H. An example of such a system is a superconductor, considered from the point of view of the phenomenological theory of superconductivity developed by Ginzburg and Landau[2].

Let such a system be found in a constant and everywhere homogeneous magnetic field H_0. In other words, H_0 represents the magnetic field which existed before the introduction of the body. The first law of thermodynamics for processes which are carried out in an electromagnetic field has the form[3]

$$\Delta E = \Delta Q - \Delta t\,\frac{c}{4\pi}\int(\mathbf{E}\times\mathbf{H})\,d\mathbf{f} \qquad (2.1)$$

Let the surface of integration extend to infinity; more accurately, we take the magnetic field on it to be equal to $\mathbf{H}_0$. Then we have

$$-\Delta t\int(\mathbf{E}\times\mathbf{H}_0)\,d\mathbf{f} = -\Delta t\int\mathbf{H}_0\,\nabla\times\mathbf{E}\,dV$$

$$= 1/c\int\mathbf{H}_0\,\Delta\mathbf{H}\,dV$$

and consequently, Eq. (2.1) can be written in the following form ($\Delta Q = T\Delta S$)

$$\Delta E = T\Delta S + \frac{1}{4\pi}\int dV\,\Delta\mathbf{H}\cdot\mathbf{H}_0, \qquad (2.2)$$

From this it follows that at constant temperature, and constant, everywhere homogeneous, magnetic field, the function has an extremum in the state of thermodynamic equilibrium.

$$\Phi(T, \mathbf{H}_0) = E - TS - \frac{1}{4\pi}\int\mathbf{H}_0\cdot\mathbf{H}\,dV \qquad (2.3)$$

Actually, $\Delta\Phi = 0$ under these conditions, in agreement with Eq. (2.2). The relations (2.2) and (2.3) were used by the author[4] in the investigation of the destruction of the superconducting state in a magnetic field.

We can raise the question as to the determination of the minimum work done by an external source on a body placed in a medium where the magnetic field is constant and homogeneous. It is not difficult to find that

$$R_{\min} = \Delta(E - T_0S) - \frac{1}{4\pi}\int \mathbf{H}_0 \Delta \mathbf{H}\, dV. \qquad (2.4)$$

Similar considerations permit us to obtain the following generalized form of (1.5):

$$(\partial H_0^i / \partial \overline{H}^i)_T > 0. \qquad (2.5)$$

Here $\overline{H}^i = V^{-1}\int H^i dV$ (V is the volume enclosed by the surface on which the magnetic field is taken to be equal to H_0). Conclusions can also be drawn from (2.5) as to the dependence of $\overline{H}$ on H_0, as was done above for the dependence of B on H.

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* Equation (1.2) permits us to determine the probability of thermodynamic fluctuations in the following manner:

$$w \sim \exp\left\{-\frac{1}{2kT}\left[\Delta T \Delta S - \frac{1}{4\pi}\int dV\,(\Delta\mathbf{H}\Delta\mathbf{B} + \Delta\mathbf{E}\Delta\mathbf{D})\right]\right\}.$$

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On the First Appearance of Atomic Electrons With l, n, n_r and $n + l$ Given

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EARLIER it was shown[1] that the expression for Z_l, the atomic number of an element [an expression obtained on the basis of the rule of systematic filling (Aufbau principle) of the $(n - l)$ groups[2]], in the electronic shell of neutral unexcited atoms of which the first electron appears with a given value for the orbital quantum number l, can be reduced to the form:

$$Z_l = {}^1\!/_6\,(2l + 1)^3 + {}^1\!/_6\,(5 - 2l). \qquad (1)$$

The second member of the right side of this equation represents a relatively small value and the dependence of Z_l on l is determined principally by the first member, which is proportional to $(2l + 1)^3$; this agrees well with the conclusions of statistical theory.[3] One can also reduce to a similar form a series of other equations[4] obtained on the basis of that same rule, equations for the first appearance of atomic electrons with a given value for the principal quantum number, for the radial quantum number and with a given value for the sum of the principal and orbital quantum numbers.

For the simplification of further exposition we shall introduce the following notation. Let

$$K(y) = {}^1\!/_6\,y^3 + \delta;\ \delta = \begin{cases} -{}^1\!/_6\,y, & \text{if } y \text{ is odd} \\ +1/3\,y, & \text{if } y \text{ is even.} \end{cases} \qquad (2)$$

From the condition $l \leq n - 1$ and from the integral value of l it follows that the maximum value of the orbital quantum number ($l_{\max}$) in the presence of the given value of $n + l$ is equal to $0.5\,(n + l - 1)$ if $n + l$ is odd and equal to $0.5\,(n + l - 2)$ if $n + l$ is even. Therefore, the number of different quantum positions in the limits of one $(n + l)$ group is equal to:[5]

$$\sum_{l=0}^{l_{\max}} 2(2l + 1) = 2(l_{\max} + 1)^2 \qquad (3)$$

$$= \begin{cases} 0.5(n + l + 1)^2, & \text{if } n + l \text{ is odd} \\ 0.5\,(n + l)^2, & \text{if } n + l \text{ is even} \end{cases}$$

From this it follows that the number of different quantum positions in the limits of an aggregate, including the $(n + l)$ groups with all the values of $n + l$ less than a certain odd number $y = 2q + 1$ $(q = 0,1,2,3,..)$ is equal to

$$\sum_{q=0}^{0.5\,(y-1)} (2q)^2 = {}^1\!/_6\,y^3 - {}^1\!/_6\,y. \qquad (4)$$

For the aggregate itself, including the $(n + l)$ groups with the values of $n + l$ less than a certain even number $y = 2q + 2$, we have, consequently,

$$\sum_{q=0}^{0.5\,(y-2)} (2q)^2 + 1/2y^2 = 1/6y^3 + 1/3y. \qquad (5)$$

By such means, taking into consideration the