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THEORY OF THE INTENSITY OF SCATTERED X-RAYS

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ABSTRACT

The writer's theory of the unmodified line in the Compton Effect (Phys. Rev., 25, 314, 1925) has recently been extended by Williams (Phil. Mag. 2, 657, 1926) and the writer (Phys. Rev., 29, 206, 1927) to the case of reflection of x-rays by crystals. Both these writers assume that it is only the  $U$  electrons (i.e. the electrons associated with unmodified scattering, see Phys. Rev., 26, 433, 1925) which take part in crystal reflection. In the present paper it is supposed that the  $U$  electrons in a given atom scatter coherently and also according to the classical theory, so that, if  $N_U$  is the number of  $U$  electrons in the atom, the intensity of the x-rays scattered in a given direction is  $N_U^2$  times the intensity scattered by a single free electron in the same direction according to Thomson's theory. In previous papers it has been assumed that the intensity of unmodified scattering is proportional to  $N_U$ . Now, however, because of the above assumptions, it is proportional to  $N_U^2$ . In modified scattering it is assumed that the  $S$  electrons (i.e. the electrons associated with modified scattering) scatter incoherently and according to the quantum theories of Compton, Jauncey and Breit. The modified scattering, as in previous papers, is, therefore, proportional to  $N_S$ , the number of  $S$  electrons in the atom. Formulas are obtained for the energy of the total (i.e. unmodified plus modified) scattering coefficient and for the ratio of the modified to the total scattering coefficient in terms of the angle of scattering, the primary wave-length and the critical absorption wave-lengths of the scatterer. The theory seems to work equally well for heavy as for light elements and explains the phenomenon of excess scattering.

It is also pointed out that Williams has made a small error in his correction for the interference of x-rays scattered by the  $U$  electrons in atoms in the same crystal plane. Rectifying this error, an excellent agreement between theory and the experimental atomic structure factors as found by Havighurst (Phys. Rev., 28, 869, 1926) for rock salt is obtained.

1. INTRODUCTION

ACCORDING to Thomson's theory<sup>1</sup> of the scattering of x-rays, the linear scattering coefficient per unit solid angle in a direction  $\phi$  with the primary rays is given by

$$s_0 = (NZ\rho/W) \cdot (e^4/m^2c^4) \cdot (1 + \cos^2\phi)/2 \quad (1)$$

where  $N$  is Avogadro's number,  $Z$  the atomic number of the scatterer,  $\rho$  its density,  $W$  its atomic weight and  $e$ ,  $m$  and  $c$  the charge and mass of the electron and the velocity of light respectively. Eq. (1) agrees fairly well with

<sup>1</sup> J. J. Thomson, Conduction of Electricity through Gases, 2nd Ed., p. 325.

experiment for moderately soft x-rays scattered by light elements at angles greater than  $60^\circ$ . When gamma rays, however, are scattered the experimental value of the scattering coefficient, which we shall denote by  $s$ , is more nearly given by

$$s = s_0 / (1 + \alpha \text{vers } \phi)^3 \quad (2)$$

as observed by Compton.<sup>2</sup> In Eq. (2)  $\alpha = h/mc\lambda$ , where  $\lambda$  is the wave-length of the primary x-rays. Eq. (2) has been derived on theoretical grounds by Compton, Jauncey and Breit.<sup>3</sup> However, for  $\lambda = 0.545\text{\AA}$  scattered by rock salt, Jauncey and May<sup>4</sup> have found for values of  $\phi$  greater than  $90^\circ$  that  $s$  is between the value given by the right side of Eq. (2) and the Thomson value,  $s_0$ . For angles less than  $90^\circ$   $s$  becomes greater than  $s_0$ , which phenomenon is known as excess scattering. This excess scattering was first observed by Crowther<sup>5</sup> and Barkla and Ayers<sup>6</sup> in the case of scattering by light elements. Later, Barkla and Dunlop<sup>7</sup> observed excess scattering when x-rays are scattered by heavy elements at  $90^\circ$ , while still more recently Jauncey and Coven<sup>8</sup> have observed this phenomenon for  $\lambda = 0.41\text{\AA}$  scattered by copper at  $110^\circ$ .

Jauncey's theory of the unmodified line in the Compton effect<sup>9,10,11</sup> supposes that unmodified scattering takes place from one set of electrons in an atom while modified scattering takes place from a second set of electrons. The electrons of the first set are said to be in the  $U$  state, while those in the second set are said to be in the  $S$  state. For brevity we shall hereafter refer to the electrons associated with the unshifted and shifted lines as the  $U$  and  $S$  electrons. Jauncey's theory gives the ratio of the number of  $U$  electrons of a given type ( $K, L, M$ , etc.) to the total number of the same type when these electrons are moving in circular orbits as<sup>12</sup>

$$\frac{N_U}{N_U + N_S} \equiv y = 0.5 - \frac{\psi}{2(2T)^{1/2}} + \frac{V}{4\psi(2T)^{1/2}} \quad (3)$$

and

$$\psi = (h/mc\lambda) \sin \frac{1}{2}\phi, \quad (4)$$

where  $mc^2V$  is the ionization energy of each electron and  $mc^2T$  is the kinetic energy of each electron in its Bohr orbit. Since  $y$  has different values for

<sup>2</sup> A. H. Compton, *Phil. Mag.* **41**, 749 (1921) and *Phys. Rev.* **21**, 483 (1923).

<sup>3</sup> A. H. Compton, *X-Rays and Electrons*, p. 305.

<sup>4</sup> Jauncey and May, *Phys. Rev.* **23**, 128 (1924).

<sup>5</sup> J. A. Crowther, *Proc. Camb. Phil. Soc.* **16**, 112 (1910).

<sup>6</sup> Barkla and Ayers, *Phil. Mag.* **21**, 275 (1911).

<sup>7</sup> Barkla and Dunlop, *Phil. Mag.* **31**, 222 (1916).

<sup>8</sup> Jauncey and Coven, *Phys. Rev.* **28**, 426 (1926).

<sup>9</sup> G. E. M. Jauncey, *Phys. Rev.* **25**, 314 (1925).

<sup>10</sup> G. E. M. Jauncey, *Phys. Rev.* **25**, 723 (1925).

<sup>11</sup> Jauncey and DeFoe, *Phys. Rev.* **26**, 433 (1925).

<sup>12</sup> Eq. (3) is in the form given by Nuttall and Williams in *Phil. Mag.* **1**, 1217 (1926). Previously the writer has used a formula where  $T = V$  which is approximately the case.

the different types ( $K$ ,  $L$ ,  $M$ , etc.) of electrons, the different  $y$ 's are distinguished by the subscripts  $K$ ,  $L$ , etc. If  $n_K$ ,  $n_L$ , etc., are the numbers of  $K$ ,  $L$ , etc., electrons per atom, then the average value of  $y$ , which we shall denote by  $\bar{y}$ , is

$$\bar{y} = \frac{n_K y_K + n_L y_L + \dots}{n_K + n_L + \dots} \quad (5)$$

Jauncey has also considered the case of scattering by electrons in elliptic orbits<sup>10</sup> and has obtained a more complicated formula than Eq. (3). The  $y$ 's for elliptic orbits, such as the  $L_1$  orbits, are supposed inserted in Eq. (5). If now it is assumed that the intensity of x-rays scattered in the direction  $\phi$  by a  $U$  electron is the same as that scattered by an  $S$  electron, then Eq. (5) gives the ratio of the unmodified scattering coefficient  $s_1$  to the total scattering coefficient  $(s_1 + s_2)$ , so that  $s_2/(s_1 + s_2) = 1 - \bar{y}$ .

Woo<sup>13</sup> and DeFoe<sup>14</sup> have tested this point experimentally and find for x-rays of various wave-lengths scattered by various elements that the experimental value of  $s_2/(s_1 + s_2)$  is always considerably less than  $(1 - \bar{y})$ . On the other hand Jauncey's theory of the unmodified line requires that when x-rays are passed through a gas in a Wilson cloud apparatus, the ratio of the number of recoil electron tracks to the number of photoelectron tracks should be  $(1 - \bar{y})\sigma/\tau$  where  $\sigma$  is the spherical scattering coefficient and  $\tau$  the true absorption coefficient. Nuttall and Williams have found good experimental agreement with this prediction.

Summing up, we may say that the evidence is that Jauncey's theory of the unmodified line agrees well with experiment for those cases where the ratio of the numbers of  $U$  electrons to the number of the  $S$  electrons is concerned; while for those cases where the ratio of the intensities of the modified and unmodified rays is concerned the agreement is only qualitative and not quantitative. An attempt to explain this latter discrepancy and to rectify it is the purpose of this paper.

## 2. INTENSITY OF X-RAYS REFLECTED BY CRYSTALS

The hint as to the explanation of this discrepancy appears in a recent paper by Williams.<sup>15</sup> Williams and independently, but later, the writer<sup>16</sup> have shown that it is necessary to take the Compton effect into account in order to explain the variation of the intensity of x-rays regularly reflected (not diffusely scattered) by crystals. Both Williams and Jauncey calculate the atomic structure factor  $F$  on the assumption that it is only the  $U$  electrons which take part in crystalline reflection. On this account therefore the effective number of electrons per atom in crystalline reflection is  $\bar{y}Z$ . However, as Compton,<sup>17</sup> Hartree<sup>18</sup> and others have shown, there is partial inter-

<sup>13</sup> Y. H. Woo, Phys. Rev. **27**, 119 (1926).

<sup>14</sup> O. K. DeFoe, Phys. Rev. **27**, 675 (1926).

<sup>15</sup> E. J. Williams, Phil. Mag. **2**, 657 (1926).

<sup>16</sup> G. E. M. Jauncey, Phys. Rev. **29**, 206 (1927).

<sup>17</sup> A. H. Compton, Phys. Rev. **9**, 29 (1917).

<sup>18</sup> D. R. Hartree, Phil. Mag. **50**, 289 (1925).

ference between the wavelets scattered (in crystalline reflection) from different electrons in the same atom. For instance Compton<sup>17</sup> has shown that if we consider only those electrons which are moving in circular orbits of radius  $a$ , the ratio of the average amplitude of the wavelet scattered by each electron in an atom to the amplitude of the wavelet scattered by a single free electron is

$$H = (\sin \xi) / \xi \quad (6)$$

where

$$\xi = (4\pi a \sin \frac{1}{2}\phi) / \lambda \quad (7)$$

Hartree<sup>18</sup> has also obtained a formula for the case where the electrons are moving in elliptic orbits and he gives tables of values of  $H$  for various values of  $\xi$ . Williams then obtains the atomic structure factor  $F$  thus:

$$F = n_K y_K H_K + n_L y_L H_L + \dots \quad (8)$$

the subscripts  $K, L$ , etc., referring to the  $K, L$ , etc., orbits. Eq. (8), however, is only justified if, when we consider circular orbits of a given radius, the  $U$  electrons can be in any position in the orbit and the orbit can be oriented in any direction. However, on reference to Jauncey's paper on the unmodified line,<sup>10</sup> it is seen that the  $U$  electrons are restricted to a certain area on the sphere of radius  $a$ . From Fig. 1 of this paper<sup>10</sup> it follows that the interference factor is only given by  $H$  when  $y$  is unity. As  $y$  approaches zero the interference factor approaches unity. Hence the writer has calculated the interference factor from the following approximate formula:

$$H' = 1 - y(1 - H) \quad (9)$$

where  $H$  is given by Hartree's tables. This formula satisfies the conditions that  $H' = 1$  when  $y = 0$  and  $H' = H$  when  $y = 1$ . The formula for the structure factor  $F$  is therefore given by

$$F = n_K y_K H_K' + n_L y_L H_L' + \dots \quad (10)$$

Hartree<sup>18</sup> gives a formula for calculating the radius  $a$  of any circular orbit. From this value of the radius it is possible to calculate  $mc^2T$ , the kinetic energy of the electron in the orbit, by equating the moment of momentum to  $kh/2\pi$  where  $k$  is the azimuthal quantum number. In this way values of  $T$  in Eq. (3) are calculated for circular orbits. For elliptic orbits  $T$  is calculated on the basis of a circular orbit of total quantum number equal to that of the elliptic orbit and then the method for calculating  $y$  for elliptic orbits according to a previous paper<sup>19</sup> is applied. However, these methods of calculating  $T$  are not applied to the outermost orbits. For these orbits it is considered best to take  $T = V$  where  $V$  is given by the ionization potential.

Havighurst<sup>20</sup> has recently obtained experimental  $F$  values for rock salt from the intensities of different orders of reflection of  $\text{MoK}\alpha$  x-rays. Havighurst's values, however, contain the Debye temperature factor. Using the

<sup>19</sup> G. E. M. Jauncey, Phys. Rev. **27**, 687 (1926).

<sup>20</sup> R. J. Havighurst, Phys. Rev. **28**, 869 (1926).

temperature factor given by Bragg, Darwin and James<sup>21</sup> and inserting the wave-length used by Havighurst, values of  $F$  without the temperature effect have been obtained and are shown in the third column of Table I. The theoretical values as calculated from Eq. (10) are shown in the fourth column. The agreement between the third and fourth columns is good.

TABLE I  
*F-values for rock salt.*

sin $\frac{1}{2}\phi$	Experiment		Theory
	Including Temperature	Excluding Temperature	
0.126	20.80	21.6	19.0
0.252	11.60	13.5	12.0
0.378	6.69	9.46	8.2
0.504	3.54	6.30	6.7

In Eq. (10) the distribution of electrons according to Stoner<sup>22</sup> is used, while the values of  $V$  in Eq. (3) are obtained from the National Research Council Bulletins written by Duane and by Compton and Mohler.

### 3. INTENSITY OF X-RAYS SCATTERED BY AMORPHOUS SUBSTANCES

Since in crystalline reflection the  $U$  electrons in an atom scatter coherently, it is now assumed that the  $U$  electrons in an atom of an amorphous substance also scatter coherently. On the other hand an amorphous substance is distinguished from a crystal by the fact that the atoms of the amorphous substance scatter incoherently while the atoms of a crystal scatter coherently. Let  $p_\nu$  be the probability that the number of  $U$  electrons in an atom is  $\nu$ , where  $\nu$  is a whole number. Assuming that the wavelets scattered by these  $U$  electrons are in phase, the amplitude scattered by each of these atoms is  $\nu$  times the amplitude scattered by a single free electron so that the intensity scattered by each of these atoms is  $\nu^2$  times the intensity scattered by a free electron. Adding the intensities scattered by the atoms with 1, 2,  $\dots$ ,  $U$  electrons in the atom, the unmodified scattering coefficient  $s_1$  is given by<sup>23</sup>

$$s_1 = s_0(1^2 p_1 + 2^2 p_2 + 3^2 p_3 + \dots + Z^2 p_Z) / Z \quad (12)$$

It is further assumed in this theory that the  $S$  electrons in an atom scatter incoherently so that for these electrons  $Z$  in Eq. (2) is replaced by the number

<sup>21</sup> Bragg, Darwin and James, *Phil. Mag.* **1**, 897 (1926).

<sup>22</sup> E. C. Stoner, *Phil. Mag.* **48**, 719 (1924).

<sup>23</sup> In crystalline reflection it is only necessary to know the average number of  $U$  electrons per atom since the amplitudes due to all the  $U$  electrons in the crystal are added. On this account the formula for the intensity of reflected x-rays (see Bragg, James and Darwin<sup>21</sup>) from an ideally imperfect crystal contains a factor  $N^2 \bar{F}^2$  where  $N$  is the number of molecules per unit volume and  $F$  is the atomic structure factor. In other words the factor is  $(NF)^2$  so that it is correct to take the average value of  $F$ . However, in scattering by amorphous substances, since we have assumed no coherence between the wavelets scattered by different atoms, the intensity contains a factor  $N\bar{F}^2$ , where  $\bar{F}$  is the root mean square of the atomic structure factor and therefore in this case it is not correct to take the arithmetical average of  $F$  as is done in crystalline reflection. In a paper read by the author at the New York Meeting of the Physical Society in 1927 the author used the arithmetical average and therefore the formula given in the abstract of that paper is only approximately correct.

of  $S$  electrons per atom. Hence  $s_2$  the modified scattering coefficient is given by

$$s_2 = (1 - \bar{y})s_0 / (1 + \alpha \text{vers } \phi)^3, \quad (13)$$

where  $\bar{y}$  is given by Eq. (5). From Eqs. (12) and (13), both  $(s_1 + s_2)$  and  $s_2 / (s_1 + s_2)$  can be obtained and compared with experiment.

The problem now reduces to finding an expression for  $p_\nu$  in terms of the  $y$ 's (as given by Eq. (3)) and also an expression for the summation,  $1^2 p_1 + 2^2 p_2 + \dots$ . Let us consider the case of a sack containing black and white balls such that the probability of drawing a white ball is  $y$ . Let us suppose that all the balls in the sack are emptied into baskets each of which contains, say, four balls. What are the probabilities that a basket will contain 1, 2, 3 or 4 white balls? The probability  $p_4$  that a given basket will contain 4 white balls is  $y^4$ . Now let the probability of drawing a black ball out of the original sack be  $z$  so that  $y + z = 1$ , then the probability of 1 black ball followed by 3 white balls being drawn is  $y^3 z$ . However, in filling the baskets it matters not in what order the balls are drawn and, since all the drawings,  $BWWW$ ,  $WBWW$ ,  $WWBW$ , and  $WWWB$ , are equally likely, the chance  $p_3$  of a basket containing 3 white balls and 1 black ball is  $4y^3 z$ . It is easily seen that  $p_2$ ,  $p_1$  and  $p_0$  are given by  $6y^2 z^2$ ,  $4yz^3$ , and  $z^4$  respectively. The  $p$ 's are therefore given by the terms in the expansion of the binomial  $(y+z)^4$ , the subscripts of the  $p$ 's being equal to the exponents of the  $y$ 's. It is easily seen that for baskets containing  $n$  balls each, the probabilities  $p_n, p_{n-1}, \dots$  are given by the respective terms of  $(y+z)^n$ . Next consider the case of two sacks, the probability of drawing a white ball from the first sack being  $y_1$  and from the second sack  $y_2$ . Now let us take  $n_1$  balls out of the first sack and  $n_2$  out of the second sack and put the  $(n_1 + n_2)$  balls in one basket. The probability  $p_\nu$  that the basket will contain  $\nu$  white balls is easily seen to be the sum of those terms in the expansion of  $(y_1 + z_1)^{n_1} \cdot (y_2 + z_2)^{n_2}$  in which the sum of the exponents of the  $y$ 's is  $\nu$ . The argument can obviously be applied to any number of sacks.

Let us return to the case of one sack and baskets containing 4 balls and denote the summation  $1^2 p_1 + 2^2 p_2 + \dots$  by  $S$ , then

$$S = 4y(y+z)^2(4y+z) \quad (14)$$

But  $y+z=1$  so that

$$S = 4y(3y+1) = 4y + 4 \cdot 3y^2 \quad (15)$$

The general formula for a basket containing  $n$  balls is

$$S = ny + n(n-1)y^2 \quad (16)$$

For the case of several sacks it can easily be shown that

$$\begin{aligned} S = & n_1 y_1 + n_2 y_2 + \dots \\ & + n_1(n_1-1)y_1^2 + n_2(n_2-1)y_2^2 + \dots \\ & + 2n_1 n_2 y_1 y_2 + 2n_1 n_3 y_1 y_3 + \dots \end{aligned} \quad (17)$$

If we replace the subscripts 1, 2, 3, etc., by *K, L, M* and give the *n*'s and *y*'s the same meanings as in Eq. (5), the unmodified coefficient is then given by

$$s_1 = s_0 S/Z \tag{18}$$

4. COMPARISON WITH EXPERIMENT

Jauncey and Coven<sup>8</sup> have measured the total scattering coefficient (*s*<sub>1</sub>+*s*<sub>2</sub>) for λ=0.41A scattered by copper at various angles, their results being shown in the second column of Table II. In the third column are shown the theoretical values calculated according to Eqs. (12), (13) and (18). Stoner's distribution of 2*K*, 2*L*<sub>I</sub>, 6*L*<sub>III</sub>, 2*M*<sub>I</sub>, 6*M*<sub>III</sub>, 10*M*<sub>V</sub> and 1*N*<sub>I</sub> electrons is used.

TABLE II  
Scattering from copper: Wave-length 0.41A.

Scattering Angle, φ	Experiment ( <i>s</i> <sub>1</sub> + <i>s</i> <sub>2</sub> )/ <i>s</i> <sub>0</sub>	Theory ( <i>s</i> <sub>1</sub> + <i>s</i> <sub>2</sub> )/ <i>s</i> <sub>0</sub>
40°	4.8	4.00
50	3.5	3.11
60	2.5	2.55
70	2.37	2.25
80	2.14	1.90
90	1.49	1.62
100	1.45	1.47
110	1.52(?)	1.36
150		1.11
180		1.04

It is seen that there is fair agreement between the second and third columns. The experimental value at 110° is doubtful.

In Table III the experimental values of *s*<sub>2</sub>/(*s*<sub>1</sub>+*s*<sub>2</sub>) as determined by Woo<sup>13</sup> and DeFoe<sup>14</sup> are given in the third column, while the theoretical values are given in the fourth column.

TABLE III  
Ratio of unmodified to total scattering.

Element, wave-length and experimenter	Angle	Experiment <i>s</i> <sub>2</sub> /( <i>s</i> <sub>1</sub> + <i>s</i> <sub>2</sub> )	Theory <i>s</i> <sub>2</sub> /( <i>s</i> <sub>1</sub> + <i>s</i> <sub>2</sub> )	1- <i>y</i>
Aluminum λ = .71A	90	0.48	0.62	.80
	105	.53	.67	.83
	120	.59	.73	.86
Woo.	135	.68	.79	.88
	150	.71	.81	.89
Copper λ = .41A	90	.55	.43	.82
	100	.63	.47	.84
	130	.84(?)	.55	.87
DeFoe				

The fifth column gives the ratio *s*<sub>2</sub>/(*s*<sub>1</sub>+*s*<sub>2</sub>) as calculated theoretically in a previous paper.<sup>10</sup> It is seen that the theory of the present paper gives values which approach closer to the experimental values than those calculated according to the method of the previous paper.

## 5. DISCUSSION

A formula for the total scattering coefficient ( $s_1+s_2$ ) has been obtained which agrees fairly well with the experimental results for copper (see Table II). The theory therefore seems to explain the phenomenon of excess scattering. However, the formulas for  $s_1$  and  $s_2$  as derived in Section 3 depend on the assumption that the wavelets scattered by the  $U$  electrons in an atom are in phase. Due to small differences of the paths of rays scattered by the various  $U$  electrons in the same atom this assumption is not quite true. A correction for partial interference should therefore be added. The interference factors calculated by Hartree<sup>18</sup> apply only to the case where the electrons are associated with crystal planes, and so cannot be used in the case of scattering by electrons in an amorphous substance. A correction might be made by using the methods of Debye<sup>24</sup> and Glocker and Kaupp<sup>25</sup> but this would complicate Eq. (12) by multiplying each term on the right side by an interference factor and so make impossible the derivation of the simple formula given in Eq. (18). The correction has therefore been omitted. The effect of the correction would be to diminish slightly the theoretical values in Table II and to increase slightly these values in Table III.

On the whole considering the evidence of Tables I, II, and III (DeFoe's values in Table III not being as reliable as Woo's values), it may be inferred that the experimental number of  $U$  electrons per atom is somewhat greater than that given by Eq. (5). From this it follows that the values calculated from Eq. (3) are somewhat too small. Since from Eq. (3) the conditions of wave-length and angle for which the unmodified line disappears<sup>19</sup> are given, it must be that the wave-length is smaller or the angle greater than the wave-length and angle given by Eq. (3) when the unmodified line disappears. An indication that this is so experimentally is given by the experiments of Woo<sup>26</sup> and Jauncey and Boyd.<sup>27</sup>

However, in spite of these small discrepancies, the writer believes that the theory as developed in this paper correlates surprisingly well the phenomena of the intensity of crystal reflection, the intensity of x-rays scattered by amorphous substances of high and low atomic numbers, the ratio of the energies of the modified and unmodified lines in the Compton Effect, and the conditions under which the unmodified line disappears.

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<sup>24</sup> P. Debye, *Ann. d. Physik*, **46**, 809 (1915).

<sup>25</sup> Glocker and Kaupp, *Ann. d. Physik* **64**, 541 (1921); see also Compton, *X-rays and Electrons*, p. 75.

<sup>26</sup> Y. H. Woo, *Phys. Rev.* **28**, 426 (1926).

<sup>27</sup> Jauncey and Boyd, *Phys. Rev.* **28**, 620 (1926).