

ATOMIC STRUCTURE AS REVEALED BY CRYSTAL REFLECTION OF X-RAYS

G. E. M. JAUNCEY

Department of Physics, Washington University, St. Louis, Missouri

In 1912 Laue discovered that crystals act towards x-rays as a three dimensional diffraction grating. W. L. Bragg simplified the mathematics of Laue's explanation of his discovery by showing that the Laue spots could be explained by reflection from the various planes in a crystal in which the atoms may be considered as being arranged. Referring to figure 1A, the white circles represent sodium atoms and the black circles chlorine atoms in a crystal of rocksalt. It is easily seen that different planes of atoms can be chosen in the crystal as represented in figure 1B. It is seen that the (100) and (110) planes in the crystal contain both chlorine and sodium atoms in each plane. Such planes may be called even planes. On the other hand there are planes like the (111) planes which contain either all chlorine or all sodium atoms in a plane—the chlorine and sodium planes alternating with each other. Such planes may be called odd planes.

Referring again to figure 1, we see that the grating space d varies according to the sets of planes considered. The Bragg law of reflection is

$$n\lambda = 2d \sin \theta \quad (1)$$

By cutting a crystal so that its face is parallel to the (100) planes and determining the angle θ for first order reflection of a known wave length, the value of d_{100} , the grating space for the (100) planes can be found. Likewise, by cutting the crystal so that its face is parallel to the (110) planes and determining the angle θ for first reflection of the same wave length, d_{110} can be found. Similarly, by cutting the crystal so that its face is parallel to the

(111) planes, d_{111} can be found. From the values of d_{100} , d_{110} , d_{111} , the crystal structure, which means the arrangement of the atoms in the crystal, may be determined. Debye and Scherrer and also Hull have devised what is known as the powdered crystal method. In this method we obtain in one and the same exposure and on one and the same photographic film a

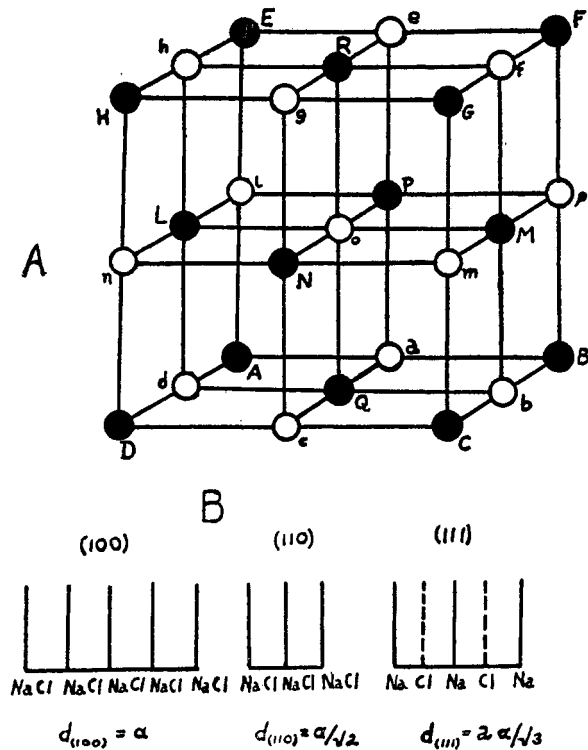


FIG. 1

record of the reflections of a given wave length from all the sets of planes. From the arrangement of the lines showing the reflections it is possible to obtain the crystal structure.

Our interest in the present paper, however, is not so much in the arrangement of the reflections as in the intensities of the various reflections. From the arrangement of the reflections the crystal

structure is found, while from the intensities we are able to get at the atomic structure, or the arrangement of the electrons in the atom. In 1921 W. L. Bragg and his pupils began a study of the intensity of the reflected x-rays in various orders and from various planes in rocksalt. The arrangement is shown in figure 2. A spectrum line of a certain wave length is isolated by the first crystal and reflected by the second crystal of rocksalt. Since rocksalt is not a perfect crystal but consists of a mosaic of small crystals whose axes make small angles with each other and since each one of the small crystals must be brought into the position to give reflection according to the Bragg law, the method used by Bragg is to rotate the second crystal slowly through the position

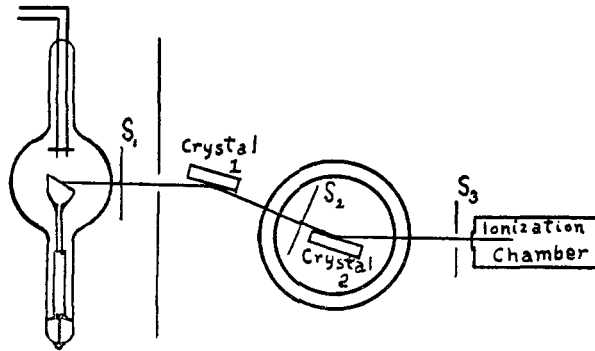


FIG. 2

of reflection with the angular velocity ω . The reflected rays enter an ionization chamber and the ionization current is registered by the electrometer. If E is the total deflection of the electrometer produced while the second crystal is rotating through the position of reflection and if I is the intensity of the rays incident on the second crystal determined by removing the second crystal and turning the ionization chamber into such a position as to receive the incident rays from the first crystal and obtaining the deflection of the electrometer in unit time, then $E \omega / I$ is known as the integrated intensity.

According to C. G. Darwin, the integrated intensity is given by

$$\frac{E \omega}{I} = \frac{N^2 e^4 F^2 \lambda^3}{2m^2 c^4 \sin 2\theta} \cdot \frac{(1 + \cos^2 2\theta)}{2 \mu} \quad (2)$$

where N is the number of molecules of sodium chloride per cubic centimeter if rocksalt is used, θ is the grazing angle of incidence at which a reflection takes place according to Bragg's law, λ is the wave length of the x-rays, e and m are the charge and mass of the electron respectively, c the velocity of light (inserted because e is in electrostatic units), μ is the linear absorption coefficient of the x-rays in the crystal and F is a measure of the diffracting power of the atom. All the quantities in equation (2) can be measured or are known except F so that equation (2) can be used to determine F . This quantity F is now known as the atomic structure factor. It should be stated here that μ is not the ordinary linear coefficient of absorption, because W. H. Bragg has shown that when a crystal is in a position to reflect x-rays its absorption coefficient is abnormally high. The increase in the ordinary absorption coefficient is termed by W. L. Bragg the extinction coefficient. Methods for the determination of the extinction coefficient are described in the papers of W. L. Bragg and also in Chapter V of A. H. Compton's "X-rays and Electrons" and will not be further discussed here. Returning to the consideration of F , it is found that when the experimental values of the integrated intensity are substituted in equation (2), and the values of F calculated, F is a function of the order of reflection and of the set of planes—(100), (110), (111) and so on—for which the integrated reflection is measured. However, since $\sin \theta$ is determined by the order of reflection and by the set of planes, F is usually given as a function of $\sin \theta$. Referring to figure 3, we see that the F values which are plotted against $\sin \theta$ fall upon two smooth curves. Curve I is obtained from the integrated reflection for the even planes, such as the (100) and (110) planes, while curve II is obtained from the integrated reflections of odd order from the odd planes such as the (111) planes. The F values obtained from the integrated reflections of even order from the odd planes fall upon the upper curve. This is because each of the even planes consists of sodium and chlorine atoms and these two types of atoms cooperate in the reflection process. Hence the F curve obtained in this case is called the (Cl + Na) curve. The odd planes, however, consist either of all chlorine or

all sodium atoms. The grating space for such planes is not the distance between one plane and the next plane but the distance from one chlorine to the next chlorine plane or the distance from one sodium to the next sodium plane. In the first order reflection, therefore, the rays reflected from the second chlorine plane

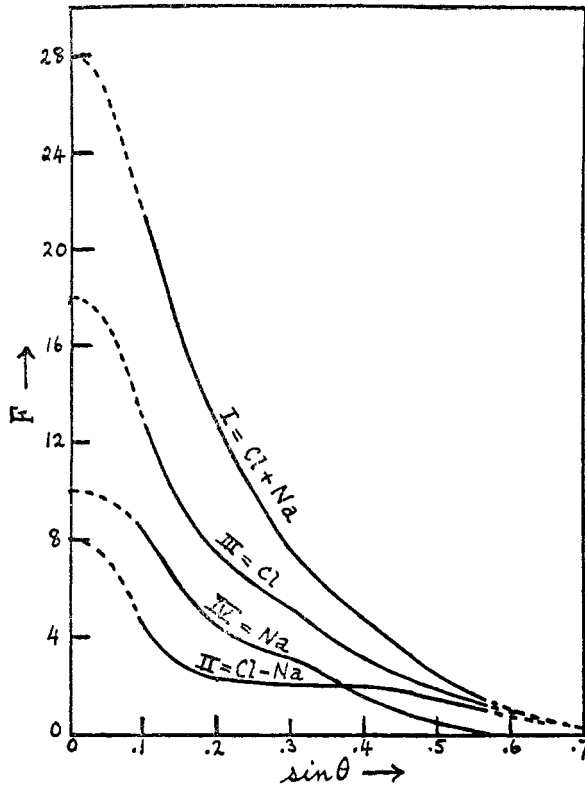


FIG. 3

are one wave length behind the rays reflected from the first chlorine plane, but in between the two chlorine planes is a sodium plane and the rays reflected from this plane are one half wave length behind the first chlorine plane and, therefore, are exactly out of phase with the rays reflected from the chlorine planes. If the reflection from a sodium plane were equally as intense as from

a chlorine plane there would be no reflection in the first order. However, reflection from the sodium planes is not as strong as that from the chlorine planes and what is observed is the difference of the intensities from the chlorine and sodium planes. The F curve obtained for this case is, therefore, called the (Cl - Na) curve. In the case of even order reflection from the odd planes the reflected rays from the sodium planes are in phase with the reflected rays from the chlorine planes and the F values for this case, therefore, fall on the (Cl + Na) curve. Obviously, if we have the F values for (Cl + Na) and for (Cl - Na), and since

$$\text{Cl} = (1/2) \{(\text{Cl} + \text{Na}) + (\text{Cl} - \text{Na})\} \text{ and } \text{Na} = (1/2) \{(\text{Cl} + \text{Na}) - (\text{Cl} - \text{Na})\} \quad (3)$$

we can obtain the F curves for Cl and Na alone. These are shown as curves III and IV respectively in figure 3. The full portions of the curves in figure 3 are obtained from experimental values of the integrated intensity, while the broken portions are extrapolations.

We shall now consider the meaning of the F curves. If the diffracting centers in the crystal were exactly in the geometric crystal planes, the F values would be constant with the angle and the F curves would be parallel to the $\sin \theta$ axis. The reason why crystals reflect x-rays and amorphous substances do not reflect x-rays is that the diffracting centers in a crystal are arranged in planes which are regularly spaced from one another while in an amorphous substance the diffracting centers are arranged at random and there are no definite planes. Any factor which tends to make the planes of diffracting centers in a crystal indefinite or diffuse will reduce the integrated intensity of the reflected x-rays and hence by Darwin's formula will make F smaller. The fact that the F curves in figure 3 are not parallel to the $\sin \theta$ axis, therefore, means that the planes are to some extent diffuse. What factors operate to cause diffuseness of the planes? Referring to figure 4, we see that if the atoms are vibrating due to their temperature then these thermal vibrations will cause the atoms to make random excursions from the geometric planes of the crystal. Imagine an instantaneous photograph taken of the crystal and the picture will be like that shown

in figure 4. The atoms will be distributed about the crystal planes as shown, some above and some below the planes. As the temperature increases the diffuseness of the planes will increase and the intensity of reflection will decrease because the crystal will become more and more like an amorphous substance. Debye has discussed this effect of the temperature on the intensity of reflection and has obtained a factor $\exp(-b \sin^2 \theta)$ for the temperature effect, where b is a function of the temperature, the specific heat of the crystal and the wave length but is a constant for a given temperature and wave length. The effect of an atom—or, rather, an electron, since it is the electrons which are

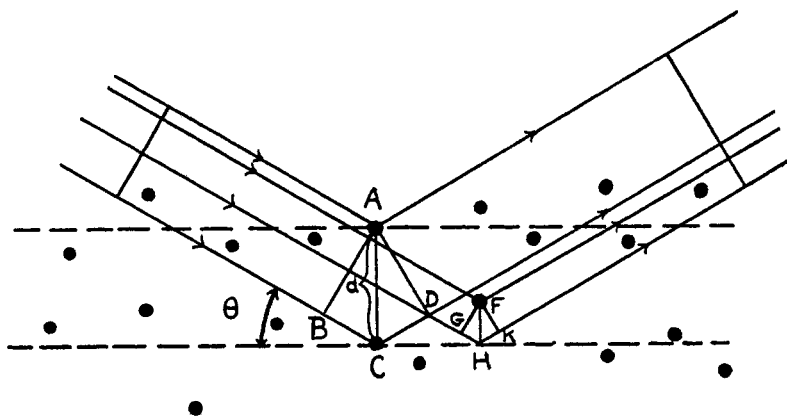


FIG. 4

the diffracting centers—being displaced from a plane is that the rays diffracted by such an electron are slightly out of phase with the rays diffracted by an electron in the plane and hence we have partial interference and a reduction of the intensity of the reflected rays and therefore a reduction of the corresponding F value. Consider the electron at F in figure 4. This is displaced a distance $FH = z$ from the geometric crystal plane. The difference of path between a ray diffracted by this electron and another ray diffracted by an electron in the plane is $2z \sin \theta$. The difference of path is therefore $(2z \sin \theta) / \lambda$ wave lengths. Since each wave-length difference of path introduces a phase difference of 2π ,

we see that the phase difference between a ray diffracted by the electron at F and another ray diffracted by an electron in the plane is $2\pi(2z \sin \theta) / \lambda$ or $(4\pi z \sin \theta) / \lambda$. Hence, the displaced electron is equivalent as far as the diffraction effect is concerned to a fraction $\cos \{ (4\pi z \sin \theta) / \lambda \}$ of an electron in the plane. If we add the values $\cos \{ (4\pi z \sin \theta) / \lambda \}$ for each electron in a cubic centimeter of the crystal and divide by the number of the molecules in a cubic centimeter, we obtain the effective number of electrons in a molecule of NaCl. Thus, in figure 3 we see that F for (Cl + Na) at $\sin \theta = 0.1$ is 21.4. This means that at this angle the molecule of NaCl which really has 28 electrons acts

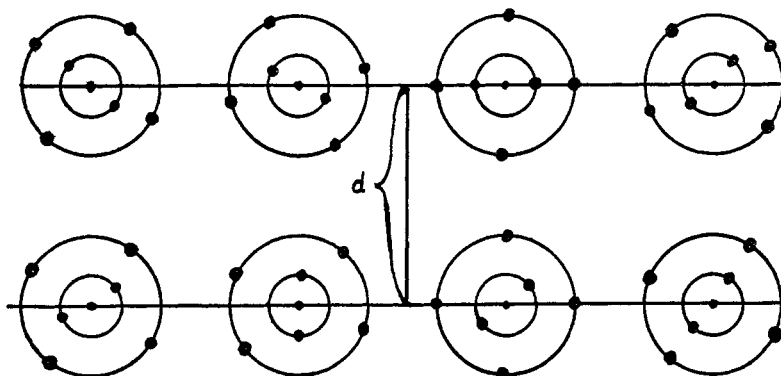


FIG. 5

as if it had only 21.4 electrons as far as reflection of x-rays at this angle is concerned. This is because the 28 electrons are not all in a crystal plane but are displaced by various amounts from the plane and due to partial interference among themselves act as if they were 21.4 electrons in a crystal plane. Similarly, the 17 or 18 electrons in chlorine act as though they were only 12.8 electrons in a crystal plane at an angle of reflection given by $\sin \theta = 0.1$.

Another factor which causes diffuseness of a crystal plane is the fact that the electrons of an atom are themselves distributed in the atom at various distances from the nucleus. It should be remarked here that the nucleus takes no observable part in

the scattering of x-rays. The effect of distribution of the electrons in the atoms is shown in figure 5, in which is shown a fictitious crystal made up of carbon atoms with 2 *K* electrons and 4 *L* electrons revolving in circular orbits. These orbits are not only in the plane of the diagram as shown in figure 5, but also may make any angle with the plane of the diagram. Obviously, this again has the effect of making the crystal planes diffuse. The diffuseness is, therefore, caused by the Debye temperature effect and by the structure of the atom. The atomic structure factor curves, or *F* curves as they are called in the literature, give us an insight into these two effects. When both effects are operative, we have $F = f \exp(-b \sin^2\theta)$ where *f* is a factor due to the structure of the atom. By comparing the *F* values at a low temperature such as that of liquid air with the *F* values at the same angles at a higher temperature, it is possible to obtain the value of *b* at the higher temperature. For reflection of molybdenum K_α x-rays ($\lambda = 0.71$ angstroms) from rocksalt at 20°C. the value of *b* is 2.39. Hence, the true atomic structure factors or *f* values can be disentangled from the temperature factor.

A. H. Compton has shown that the true atomic structure factor or *f* value for an electron moving in a circular orbit of radius *a* is

$$\frac{\sin \{(4\pi a \sin \theta)/\lambda\}}{(4\pi a \sin \theta)/\lambda}$$

If this is summed for each electron in the atom, we obtain the *f* value for the atom. Or working backwards, if we measure an *F* value then after correcting for the temperature factor we can use the formula to obtain *a*, the radius of the orbit. Of course, this is for an ideal case of an atom with only *K* electrons. In the actual case, the electrons are not all in one orbit, and the problem is more complicated. For electrons in two different orbits such as *K* and *L* circular orbits, assuming that we know the numbers of electrons in each orbit, we could by finding the *F* values for two values of $\sin \theta$ and thence obtaining the *f* values calculate the radii of the *K* and *L* orbits. However, the actual problem is even more complicated than this, because the orbits are not all

circular but some orbits are elliptical and perhaps even more complicated than elliptical. Also, we do not know the numbers of electrons in each group of electrons. However, if we take enough F values at enough different angles, we are able to solve the problem. Duane and later A. H. Compton have given us a general method for analyzing the F values and obtaining therefrom the structure of the atom. This method is known as the Fourier analysis method because it makes use of the same mathematical

TABLE 1
F values in the electron distributions of Cl and Na
D = 3.25 ångstroms
 sin θ for first order = 0.109

<i>n</i>	<i>F_n</i>		<i>n</i>	<i>F_n</i>	
	Cl	Na		Cl	Na
1	13.60	8.80	5	2.10	0.10
2	7.84	5.46	6	1.15	0.00
3	5.15	3.05	7	0.31	
4	3.40	0.72			

principle as used in analyzing any periodic motion into its constituent simple harmonic motions. The formula for it is as follows:

$$U = (8\pi r/D^2) \sum_{n=1}^{n=\infty} n F_n \sin(2\pi nr/D) \quad (4)$$

where Udr is the number of electrons between two spheres of radii r and $r + dr$, the centers of the spheres being at the center of the atom, F_n is the atomic structure factor for the n th order reflection from a set of planes whose grating space is D , and r is the distance from the center of the atom. U is called the radial distribution of the electrons in the atom and is usually given in electrons per ångstrom. It will be noticed that the right side of equation (4) is a summation of a series. It is a very cumbersome formula and the labor of applying it is such that a calculating machine is necessary. In making the calculations for U it is often more convenient to use values of F_n read off from the F

curves of figure 3 rather than the experimental F values. This is justifiable so long as the F values are read off at equal increments of $\sin \theta$, for instance, at $\sin \theta = 0.1, 0.2, 0.3$, and so on, respectively. However, when this is done, a fictitious value of the grating space D must be used. The F values used in the calculation of the electron distributions in chlorine and sodium are shown in table 1.

These are values obtained by Havighurst when molybdenum K_α x-rays are reflected from rocksalt. From these values Havighurst obtains the electron distribution, or U curves shown in

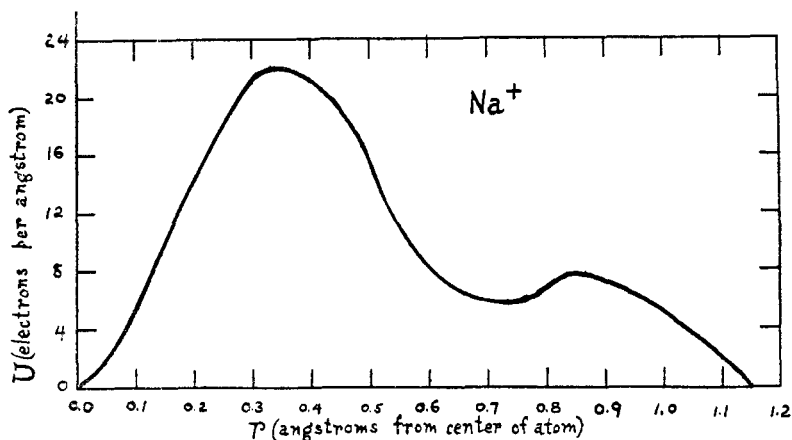


FIG. 6

figures 6 and 7. In table 1, the values of F_6 and F_7 for chlorine and of F_5 for sodium are extrapolated. This fact, therefore, introduces some uncertainty into the U curves shown in figures 6 and 7. The position of the maximum of each of the humps gives the distance of each different group of electrons from the center of the atom, while the area under each of the humps gives the numbers of the electrons in the respective groups. Thus, in the sodium atom there are 8 $K + L$ electrons at 0.33 angstrom and 2 L electrons at 0.85 angstrom from the center of the atom. In the chlorine atom, there are 10 $K + L$ electrons at 0.27 angstrom, 5 M_{III} electrons at 0.75 angstrom and 3 M_{I} electrons at

1.22 angstroms from the center of the atom. The K and L electrons are merged together because of the heat vibrations. If D in equation (4) is made indefinitely great and the increments of $\sin \theta$ indefinitely small, the right side of equation (4) takes the form of a Fourier integral. Applying the Fourier integral method of analysis to the temperature factor alone, Mr. Claus of Washington University and the writer have found that the most probable displacement of the heat vibrations is 0.175 angstrom. Since the radii of the K orbits for both sodium and chlorine are thought to be much less than 0.175 angstrom, the effect of the thermal vibrations is to obliterate any evidence for a separate K orbit in these analyses. The thermal vibrations have the

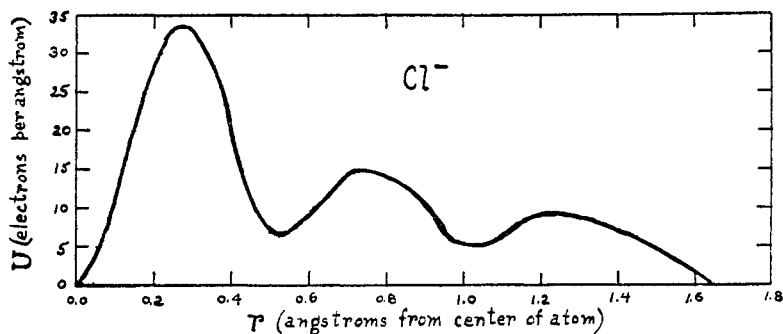


FIG. 7

further effect of broadening the humps due to the L and M electrons, and of shifting the maxima somewhat further out from the center than is the true distance of the L and M electrons from the center of the atom. It should be remarked here that a U curve gives the electron distribution relative to the average center of the atom, the true center of the atom vibrating about the average center due to the temperature effect and carrying the electrons with it.

The exact interpretation of the F curves is still in the process of being worked out. It seems to the writer that the Compton effect must somehow be taken into account. In fact, the F curves as given by Havighurst have a shape which cannot be

obtained from the classical theory while the whole of this present paper is based on the classical theory. The situation at the time of writing this paper is that more work is needed on the experimental side in order to obtain more accurate F values and also on the theoretical side to show definitely what effect, if any, the Compton effect, which has to do with the change of wave length on the scattering of x-rays, has on the Fourier analysis method and the resulting electron distribution curves. Nevertheless, the writer believes that the method of unravelling atomic structure as outlined in this paper has great promise of being one of the most useful and direct means of adding to our knowledge of the inside of the atom.

REFERENCES

- P. DEBYE, *Ann. der. Physik.*, **43**, 49 (1914).
C. G. DARWIN, *Phil. Mag.*, **27**, 315 and 675 (1914).
A. H. COMPTON, *Phys. Rev.*, **9**, 29 (1917).
BRAGG, JAMES AND BOSANQUET, *Phil. Mag.*, **41**, 309 and **42**, 1 (1921).
C. G. DARWIN, *Phil. Mag.*, **43**, 827 (1922).
W. DUANE, *Proc. Nat. Acad. Sci.*, **11**, 502 (1925).
J. A. BEARDEN, *Phys. Rev.*, **27**, 796 (1926).
BRAGG, DARWIN AND JAMES, *Phil. Mag.*, **1**, 897 (1926).
R. J. HAVIGHURST, *Phys. Rev.*, **28**, 869 and 882 (1926); **29**, 1 (1927).
G. E. M. JAUNCEY, *Phys. Rev.*, **29**, 757 (1927).
JAMES AND FIRTH, *Proc. Roy. Soc., A*, **117**, 62 (1927).
WALLER AND JAMES, *Proc. Roy. Soc., A*, **117**, 214 (1927).
R. J. HAVIGHURST, *Phys. Rev.*, **31**, 16 (1928).
JAUNCEY AND CLAUS, *Phys. Rev.*, **31**, 717 (1928).
JAUNCEY AND CLAUS, *Phys. Rev.*, **32**, 12 (1928).
A. H. COMPTON, *X-Rays and Electrons*, Chapter V.