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THE STRUCTURE OF SOFT X-RAY LINES

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Abstract

The experimental work on soft x-rays has shown that the lines produced by the bombardment of a solid target are much broader than those emitted by a vapor. This is due to the fact that the upper level is not sharp. The breadth and the shape can be calculated from the various models which have been used for describing the behavior of electrons in metals. The free electron model gives a line which has a sharp edge on the short wave-length side. This is not observed in Be. The calculated width, however, agrees well with the observed. The bound electron model gives a more satisfactory shape for Be, but the width cannot be exactly determined. The comparison of the line shapes calculated on the basis of these two models with that observed in Be shows that, although the free electron model gives a good approximation to the zero point energy, the distribution of energy levels is strongly affected by the periodic potential in the crystal.

THE experimental work on very soft x-rays and on far ultraviolet spectra has shown that although there is a correlation between the lines of these two types, there are also outstanding differences. The lines emitted by an excited vapor, such as is produced by a hot spark discharge, are sharp lines of the type ordinarily found in optical spectra. On the other hand, lines in the same region, when produced by bombardment of a solid target, are found to have a very considerable width, and to be displaced from their position as observed in the hot spark.[1] To give an explanation of this fact one must remember that the x-radiation is emitted during a transition between stationary states of the solid body, while with the source in the vapor state, the transition is between states of a single atom. That this can be neglected in the treatment of the ordinary x-ray spectra is due to the fact that the very low levels of an atom are practically undisturbed when the atom becomes part of a crystal.

In terms of the model in which the interaction between electrons is not explicitly considered, and in which each electron moves in a potential field due to the nuclei and all the other electrons, the process of excitation and emission of a soft x-ray line may be described as follows. The excitation con-

[1] Ericson and Edlen, Zeits. f. Physik **59**, 656 (1930); M. Soderman, Zeits. f. Physik **65**, 656 (1930).

sists in the removal, by the bombarding electron, of another electron from one of the low levels of the target. In the case of low levels it may equally well be said that the electron is removed from one of the low levels of a particular atom in the target. This electron may be put into one of the unoccupied upper states of the crystal, or it may be entirely ejected. The emission of the x-ray then takes place when an electron from an upper state falls into the vacant lower state. If this electron comes from one of the highest group of ordinarily occupied states, that is from the group of states occupied by the valence electrons, it may have had any one of a large number of energies in this initial state. On this account the observed line will consist of a large number of superposed lines which blend together to give a wide band. The width and the shape of this band are determined by the distribution in energy of the upper levels as well as the distribution of transition probabilities. In case the lower state is one of a group of levels whose energies differ somewhat among themselves, this too must be taken into account. In most cases accessible to observation this is probably negligible. These observations, then, furnish a convenient means of checking experimentally the energy level distribution required by the various models for the behavior of electrons in metals.

The work of Söderman on Be furnishes a good example of what may be done in this direction.

The Free Electron Model

The model used by Pauli, Sommerfeld,[2] and others assumes that the outstanding characteristic of the valence electrons is their ability to move more or less freely through the crystal. The wave functions given by this model, as well as the distribution of energy values are given by Sommerfeld. The total number of stationary states whose energies lie between E and $E+dE$ is proportional to $E^{1/2}dE$. For ordinary temperatures, the temperature energy is so small compared with the zero point energy that it may be neglected. In this case, all of the energy levels up to those having the critical energy $\overline{E}=(h^2/2m)(3n/8\pi)^{2/3}$ will be occupied, and all those states having higher energy will be empty. In this expression for the critical energy, h is Planck's constant, m is the mass of an electron, and n is the number of free electrons per cubic centimeter.

In Be the electrons which occupy the L levels in the atoms will form the group of free electrons in the metal. It is then necessary to find the transition probability between one of these "free" states and an unoccupied K state. This can be found in the usual way from the knowledge of the functions. When averaged over all possible relative positions of the K function and the "free" function, the square of the amplitude of the electric moment turns out to be

$$M^2 = DE/(h^2Z^2/8\pi^2ma_0^2 + E)^6 \qquad (1)$$

D is a constant whose value is not essential, since only the dependence on E

[2] W. Pauli, Zeits. f. Physik **41**, 81 (1927); A. Sommerfeld, Zeits. f. Physik **47**, 1 (1928).

affects the shape of the x-ray line. The fact that the transition probability depends only on E and not on the direction of motion of the free electron is due to the spherical symmetry of the K function. In Eq. (1) Z is the effective nuclear charge which determines the extent of the K function, a_0 is the radius of the first Bohr orbit, while the other symbols have their usual significance. The combination of the transition probabilities with the distribution of energy levels gives for the shape of the emitted line

$$I \sim E^{3/2}/(h^2Z^2/8\pi^2ma_0^2 + E)^6 \tag{2}$$

from $E=0$ to $E=\overline{E}$. In this expression the ν^4 factor is neglected since the width of the line is only a small part of its total frequency.

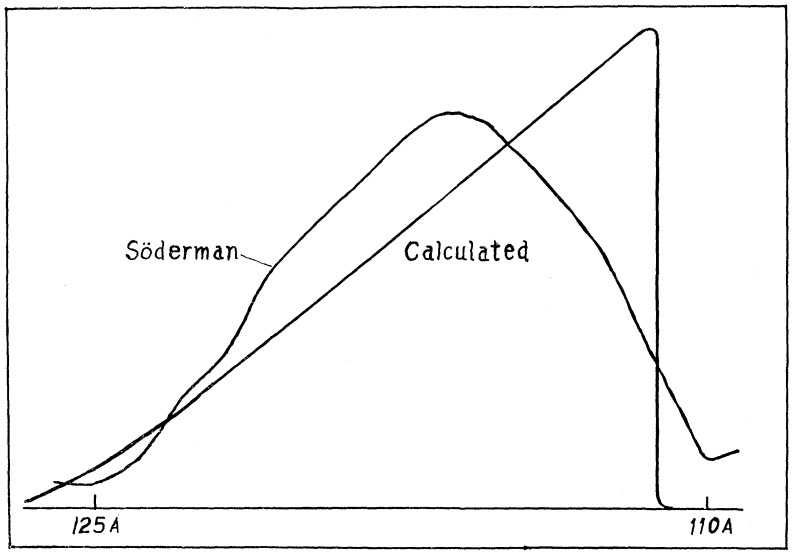

Fig. 1. Comparison of line observed in Be with that calculated from the free electron model.

Fig. 1 shows the agreement of this calculated curve with the observations of Söderman for Be. The width is calculated on the basis of two free electrons per atom. The height of both curves is of course arbitrary. The distinctive feature of the free electron model is the sharp edge on the short wave-length side. This does not appear in the observations, although there is a certain amount of asymmetry to be seen. The calculated width agrees very well, however, with that observed.

The Bound Electron Model

The other model for which calculations can readily be made is that introduced by Bloch.[3] From this point of view each electron is initially attached to a particular atom, but can easily jump to an adjacent atom under the influence of an external field. In this case the spread of the energy levels is pro-

[3] F. Bloch, Zeits. f. Physik **52**, 555 (1928).

duced by the perturbation of the electron by the surrounding atoms. The energy of a stationary state is given by Bloch to be

$$E_{lmn} = E_0 + \alpha - 2\beta\{\cos(2\pi l/G_1) + \cos(2\pi m/G_2) + \cos(2\pi n/G_3)\} \quad (3)$$

E_0 is the energy of the electron in the field of its own nucleus only. α is the electrostatic perturbation of the adjacent nuclei and electrons, while β is the exchange integral. l, m, and n are integers which designate the state and may have values such that the arguments of the cosines range between $-\pi$ and $+\pi$.

The number of energy levels lying between E and $E+dE$ is very difficult to evaluate analytically, but a rough graphical integration gives the form in-

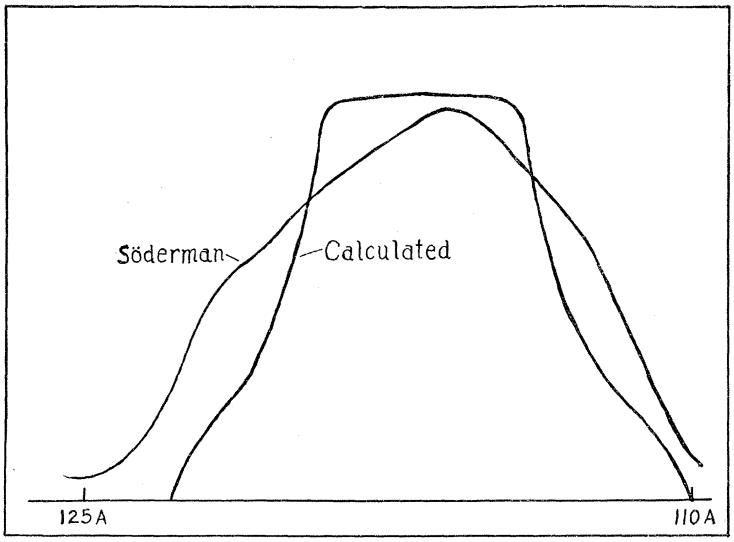

Fig. 2. Comparison of line observed in Be with that calculated from the bound electron model of Bloch.

dicated in Fig. 2. The width of the group of levels depends upon the value of the integral β. For the curve shown in Fig. 2 the functions suggested by Slater[4] were used in evaluating this integral. Each atom was assumed to have six effective neighbors, and their distance was determined from the density as if the crystal had a simple cubic lattice. In this model the transition probability is about the same for all states since it is essentially the transition probability from an L state to a K state. Although the theoretical determination of the width is subject to a number of uncertainties, the figure shows that it is of the right order of magnitude. The shape of the curve agrees roughly with the observations.

[4] J. C. Slater, Phys. Rev. **36**, 57 (1930).

Discussion

The distinctive difference between the two theoretical curves lies in the sharpness at the short wave-length edge. In each case the Pauli exclusion principle, or the Fermi statistics, causes all of the states whose energy is less than a certain critical amount to be occupied, and all others to be empty. In the free electron model the density of states increases continually with the energy, so that there is a sharp edge. The other model, which takes some account of the periodic variations of potential within the crystal, indicates that the density of the states is not a monotonic function of the energy, but consists of a series of maxima which roughly correspond to the various types of state in the free atom. In case the outer shell of the atom is closed, as is the case with Be, the end of the occupied states falls at a minimum and does not produce a sharp break. On the other hand, an element such as Li should have a sharp edge on its lines, since there are only enough electrons to fill up half of the states in the first group. The observed shape of the curve indicates that in Be the potential variations do produce a considerable effect on the distribution of the energy levels.

In all of these calculations the lower level has been treated as single since a rough calculation shows that it will be much narrower than the upper level.

The operation of the Pauli exclusion principle is clearly seen in the fact that the lines have any width at all. If the classical statistics were applicable all of the electrons would be in states at or near the lowest value of the energy.