SATELLITES OF X-RAY SPECTRA

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A mechanism is proposed to explain the appearance of multiply ionized atoms; it is similar to auto-ionization of atoms in β-decay. The calculated intensities of the x-ray Kα and some Kβ satellites are in agreement with the experimental data. It is shown that nonradiative transitions influence significantly the relative intensity of the KL_I and $KL_{II\ III}$ satellites. The effect of chemical bonding on the satellite intensity is considered.

THE nature and properties of many classes of x-ray satellites, unlike those of the main lines, remain at present unclear. In addition to the importance of solving these problems for x-ray spectroscopy, a careful study of satellites allows one apparently to obtain valuable information on the ionization mechanism of the inner shells of atoms, on the phenomena accompanying this process, and also on the behavior of electrons in a solid. An attempt is made in this paper to study the properties and to explain the nature of some types of satellites; this attempt is based on the concept of auto-ionization of the atom when the number of inner electrons changes.

According to the theory of multiple ionization,[1,2] the short-wavelength Kα satellites are emitted by atoms which lack, besides the K electron, also one or several L electrons (atoms lacking K, L, K and L, etc., electrons will be referred to below as K, L, and KL ionized). The effective cross-sections for the KL ionization of an atom under electron excitation have been calculated by Richtmyer [3] in the Born approximation. However, no allowance was made for the effect of Auger transitions on the relative intensity of the satellites, nor do the results of Richtmyer [3] explain the presence in the secondary spectrum of satellites which are practically as intense as those of the primary spectrum. This circumstance makes it possible to propose a single mechanism for the appearance of multiple ionization by both electron and photon excitation of the atom. The mechanism proposed in this paper is analogous to the auto-ionization of the atom in beta decay, considered by Migdal [4] and Feĭnberg [5] in the approximation of sudden perturbations. The corresponding relations have in fact been used by Bloch [6] in the calculation of the probability of KM ionization.

The relative intensity κ of the Kα satellites is commonly measured at excitation energies larger than the energy E_K of the K level by a factor of 3—5, because then κ no longer depends on the excitation energy. One can therefore assume that the energy of the exciting photon $\hbar\omega \gg E_K$. The removal of the K electron from the atom upon absorption of a photon leads then to such a rapid change in the potential for the L electrons that the approximation of sudden perturbations becomes applicable to them. Indeed, the condition of suddenness will be fulfilled if the time of escape of the K electron outside the bounds of the L shell will be small compared with the periods of the L electrons:

$$a/v \ll \hbar/E_L, \tag{1}$$

where a is the effective radius of the L shell, v the velocity of the emitted K electron, and E_L the energy of the L electron. Since

$$E_L = Z_L e^2/a,$$

where Z_L is the effective charge for the L electrons, we have from (1)

$$Z_L e^2/\hbar v \ll 1. \tag{2}$$

Thus, in the case considered, the condition for the applicability of sudden perturbations coincides with the condition for the applicability of the usual Born approximation.

Expressions (1) and (2) can readily be brought to a form more convenient for numerical estimates by taking into account that

$$E_L \sim Z_L^2, \qquad v \sim (\hbar\omega)^{1/2}.$$

Then we obtain from (1) and (2)

$$2\sqrt{E_L/\hbar\omega} \ll 1. \tag{3}$$

One can assume that for $\hbar\omega = (3-5)E_K$ condition (3) is already sufficiently well fulfilled, since the ratio E_L/E_K for not too large Z is of the order of 10^{-1}. It can thus be assumed that the approximation of sudden perturbations can be applied in considering the relative intensity of Kα satellites.

In accordance with the approximation of sudden perturbations, the probability of a transition of the system from the state ψ_k^0 of the unperturbed Hamiltonian to the state ψ_n of the perturbed one is given, for a perturbation which is not small, by the expression [7]

$$W_{kn} = \left| \int \psi_k^0 \psi_n^* \, d\tau \right|^2. \qquad (4)$$

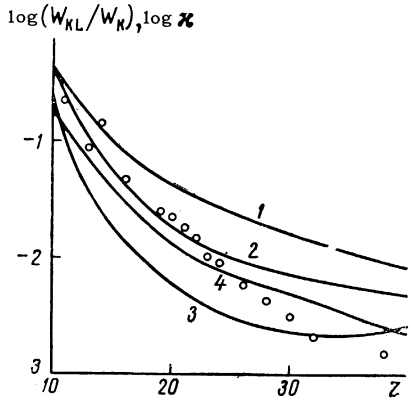
This formula was used to calculate the probability of KL ionization of a potassium atom, for which Hartree [8] and Thatcher [9] calculated self-consistent wave functions without exchange for the normal atom and the K and L ionized atoms. Since the angle parts of such functions are chosen in the form of the common spherical functions, the selection rules for l and m are found from (4) to be $\Delta l = 0$ and $\Delta m = 0$. Inasmuch as the functions from [8,9] with equal l are not orthogonal and the integral in (4) is a coefficient of the expansion of ψ_k^0 in the orthogonal system of functions ψ_n, the functions from [8,9] with equal l were additionally orthogonalized. It turned out that $W_{2p,2p} = 0.99448$ and $W_{2s,2s} = 0.98446$. The difference between unity and these values will determine the transition probability of a 2p or 2s electron to any other state of the perturbed Hamiltonian. From this difference one must, however, subtract the probability of the 2p → 3p, 2s → 1s, and 2s → 3s transitions which cannot occur in potassium by virtue of the fact that the corresponding states are occupied. The probabilities were also calculated according to (4) with orthogonalized functions from [8,9] and turned out to be: $W_{2p,sp} = 0.00176$, $W_{2s,3s} = 0.00135$, and $W_{2s,1s} = 0.00053$.

The probability $W_{n,r}^{(q)}$ of removing any q electrons out of a total of r present in the nl subshell was found from the formula

$$W_{nl,r}^{(q)} = C_r^q W_{nl}^q (1 - W_{nl})^{r-q}, \qquad (5)$$

where W_{nl} is the probability of removing one electron from the nl subshell and C_r^q is the binomial coefficient. For potassium $W_{2p} = 0.00376$, $W_{2s} = 0.01366$, $W_{2p,6}^{(1)} = 0.02214$, and $W_{2s,2}^{(1)} = 0.02695$.

In order to obtain the dependences of $W_{2p,6}^{(1)}$ and $W_{2s,2}^{(2)}$ on the atomic number Z, the probabilities $W_{2p,2p}$ and $W_{2s,2s}$ were also calculated in the approximation of hydrogen-like wave functions with a Slater effective charge. One may hope that despite the crudeness of such an approximation, the obtained dependence of the quantities $1 - W_{2p,2p}$ and $1 - W_{2s,2s}$ on Z (which turned out to be close to $Z^{-2.4}$) does not differ too much from the real dependence. The hydrogen-like functions did not turn out to be suitable for a direct calculation of the probabilities $W_{2s,1s}$, $W_{2s,3s}$, and $W_{2p,3p}$. One can, however, show that accurate to terms of the order of Z^{-3} the Z dependence of these probabilities coincides with the Z dependence of the probabilities $1 - W_{2p,2p}$ and $1 - W_{2s,2s}$. Therefore the values of all the probabilities for various Z were found by extrapolating the $Z^{-2.4}$ curve for potassium. The probabilities $W_{2p,r}^{(1)}$ and $W_{2s,r}^{(1)}$ were calculated from formula (5) with account of the filling of the 3s subshell for $10 \leq Z \leq 12$ and of the 3p subshell for $12 < Z \leq 18$. The results are presented in the figure (curve 1).



Dependence of the relative intensity of Kα satellites on Z. Curve 1 – relative probability of KL ionization; curve 2 – total theoretical relative intensity of the Kα satellites; curve 3 – theoretical relative intensity of KL_I satellites; curve 4 – theoretical relative intensity of the $KL_{II\ III}$ satellites. The points are the experimental values of the ratio of the intensity of Kα satellites to the intensity of the $K\alpha_{1,2}$ doublet according to[11].

The ratio of the intensity of the Kα satellites to the producing line—the relative intensity κ—is given by the expression

$$\varkappa = \frac{N_{KL}}{N_K} \frac{P_{KL}}{P_K}, \qquad (6)$$

where N_K and N_{KL} are the numbers of K and KL ionized atoms, and P_K and P_{KL} are the probabilities of radiative filling of a hole on the K level in K and KL ionized atoms. A calculation of the ratio of probabilities of radiative 2p → 1s transitions for K and KL ionized potassium atoms from the usual formulas for the probability

of spontaneous dipole transitions with wave functions from [8,9] gave a value of 1.02. In view of its closeness to unity and the obviously weak dependence on Z, it is assumed below to be equal to unity. But in $KL_{II\ III}$ ionized electrons, emitting $KL_{II\ III}$ satellites, unlike in KL_I ionized atoms emitting KL_I satellites, the number of electrons which can go over to the K level is one less. It can therefore be assumed that $P_{KL_I} = P_K = (6/5)P_{KL_{II\ III}}$.

The ratio N_{KL}/N_K was obtained assuming that the numbers N_K, N_{KL_I}, and $N_{KL_{II\ III}}$ are dynamically constant. In this case, the relative numbers N_K, N_{KL_I}, and $N_{KL_{II\ III}}$ will be expressed by the formulas

$$N_{KL_I} = \frac{W^{(1)}_{2s,r}}{\Gamma_{L_I} + \Gamma_{K'}}, \qquad N_{KL_{II\ III}} = \frac{W^{(1)}_{2p,r} + N_{KL_I}\Gamma^C_{L_I}}{\Gamma_{L_{II\ III}} + \Gamma_{K''}},$$

$$N_K = \frac{1}{\Gamma_K}[(1 - W_{2p})^6(1 - W_{2s})^2 + N_{KL_I}\Gamma^0_{L_I} + \Gamma_{L_{II\ III}}N_{KL_{II\ III}}]. \qquad (7)$$

Here Γ_K is the total width of the K level; $\Gamma_{K'}$ is the partial width of the KL_I level, corresponding to probability of filling the hole in the K shell by radiative and Auger transitions. $\Gamma_{K''}$ is the same for the $KL_{II\ III}$ level; $\Gamma^0_{L_I}$ is the partial width of the KL_I level corresponding to the probability of filling a hole in the L_I shell by radiative and Auger transitions, and $\Gamma_{L_{II\ III}}$ is the same for the $KL_{II\ III}$ level: $\Gamma^C_{L_I}$ is the partial width of the KL_I level corresponding to the probability of filling a hole in the L_I shell by means of Coster-Kronig transitions (Coster-Kronig transitions are a modification of Auger transitions for which the initial states of two electrons and one final state belong to the same shell). In addition, $\Gamma_{L_I} = \Gamma^0_{L_I} + \Gamma^C_{L_I}$.

In deriving (7), the KL_{II} and KL_{III} levels were not differentiated, and the KM and KN etc. ionized atoms were identified with K ionized atoms. At present practically no data are available on the Coster-Kronig widths and yields of the L_I level for $Z < 50$. For this reason, the following assumptions were made: Γ_{L_I} and $\Gamma_{L_{II\ III}}$ increase linearly with Z starting with $Z = 12$, and reach 4 and 1.5 eV for $Z = 29$ and $Z = 30$ respectively. The 1.5 eV value agrees with data on the widths of $L_{II\ III}$ levels.[10] The Coster-Kronig yield for the L_I level for all $Z < 30$ is constant and equal to 0.8. For $Z \geq 30$ the quantities $\Gamma^0_{L_I}$ and $\Gamma_{L_{II\ III}}$ continue to increase linearly, and $\Gamma^C_{L_I}$ decreases linearly to zero at $Z = 50$ in correspondence with the gradual forbiddeness of Coster-Kronig transitions from the L_I level in the Z interval from 29 to 50. Finally, it was assumed that $\Gamma_{K'} = \Gamma_{K''} = \Gamma_K$. The values of Γ_K were taken from[10].

The results of the calculations of the relative intensity κ are given in Fig. 2. The points refer to the experimental values of the relative intensities of the group of satellites $K\alpha_4$, $K\alpha_3$, $K\alpha'_3$, and $K\alpha'$ according to Parratt.[11] The theoretical and experimental data are in good agreement for small Z up to $Z = 24$. The discrepancy for large Z can be attributed to the approximations made in obtaining $\kappa(Z)$ (particularly, approximations made in estimating the probability of nonradiative transitions). In addition, preliminary calculations indicate that for Z on the order of 30—40 some of the $K\alpha$ satellites are superimposed on the $K\alpha_1$ line. Thus only part of the $K\alpha$ satellite intensity is registered experimentally for these values of Z; this leads to a decrease of the experimental values of κ.

The foregoing calculations of the relative intensity of the satellites are, strictly speaking, correct for free atoms. For atoms in a solid the relative intensity should to some extent depend on the chemical bonding for two reasons: first, the probability of the ejection of an L electron depends on the wave function of the final state which, for an atom in a solid, is a state of one of the unfilled energy bands and which depends on the type of chemical bonding; second, a change in the chemical bonding changes the probability of the Auger transitions which, as shown above, affect the relative intensity of the satellites appreciably. The effect of the chemical bonding should be strongest for light elements and should decrease with increasing Z as the L level is transformed into an inner level; this is indeed observed. Thus a study of the $K\alpha$ satellites can in principle yield information on the characteristics of the chemical bonding.

Obviously KL ionization should and does give rise to the appearance of satellites of the $K\beta_1$ line. However these satellites have an energy higher than that of the K absorption edge. Therefore their experimental values are decreased appreciably by self-absorption. This did not make it possible to compare in this work the experimental and theoretical data on these satellites.

The satellites of the K lines emitted by KM ionized atoms can be similarly considered. Condition (3) is considerably better satisfied for M electrons since the ratio E_M/E_K is of the order of 10^{-2} for not too large Z. Calculations of the

probability of KM ionization for potassium according to (4) and (5) with the functions from [8,9] gave the following values: $W^{(1)}_{3S,2} = 0.059$ and $W^{(1)}_{3p,6} = 0.138$. The Z dependence of KM was calculated with the aid of hydrogen-like wave functions and turned out to be $\sim Z^{-3.6}$ for $Z \geq 18$.

KM ionization leads to the appearance of the corresponding satellites for the $K\alpha$ and $K\beta$ lines. As Deslattes has shown,[12] for gaseous argon, and for potassium and chlorine in KCl, the short-wavelength components of the $K\beta$ group are emitted by KM ionized atoms with relative intensities (relative to the $K\beta_{1,3}$ doublet) of 0.29, 0.40, and 0.19 respectively for Ar, Cl^-, and K^+. A calculation of the same intensities using the calculated KM-ionization probabilities yields the values 0.28, 0.42, and 0.20 respectively. Parratt [11] observed the satellite $K\alpha''$, whose excitation potential is close to the KM ionization energy for $16 \leq Z \leq 24$. However the difficulties connected with the separation of such satellites from the short-wavelength branch of the $K\alpha_1$ line do not allow one to carry out a precise determination of their relative intensity.

With changing number of K electrons there is a definite probability of the ejection of two or more L or M electrons. This probability can be calculated from formulas (1) and (2) if the interaction of the ejected electrons is neglected. In this case the intensity of the corresponding satellites ($KL^{(2)}$ or $KM^{(2)}$ satellites) is, roughly speaking, less than the intensities of the $KL^{(1)}$ or $KM^{(1)}$ satellites by as much as these are less than the intensity of the producing lines. In addition, the Z dependence of the relative intensity $\kappa^{(2)}$ will in first approximation be determined by the square of $\kappa^{(1)}(Z)$, i.e., $\kappa^{(2)}(Z)$ will decrease rapidly with increasing Z. However, since for $Z \approx 10$ the value of $\kappa^{(1)}$ is of the order of 0.2, type $KL^{(2)}$ and $KM^{(2)}$ satellites can be observed for atoms with small Z. Indeed, many short-wavelength satellites are observed for these elements, their number decreasing very rapidly with increasing Z; their identification remains so far unclear.

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