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PHYSICS

1968

SovietRxiv

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UDC 539.26

PHYSICS

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ON THE MECHANISM OF THE ORIGIN OF THE K_{β_5} LINE OF THE X-RAY SPECTRUM OF 3d-METALS

(Presented by Academician G. V. Kurdyumov, January 18, 1968)

In connection with the intensive search for new materials possessing properties required for various fields of technology, the development of accurate ideas about the electronic structure of transition metals and alloys based on them is acquiring special importance. In the literature there still exist considerable discrepancies in viewpoints concerning the origin of the last emission line of the x-ray spectrum of 3d-metals, which reflects the structure of the valence electron band responsible for chemical bonding. More often than others, the concept has been expressed that this line, owing to the increased density of levels of d-symmetry (approximately 20 times, compared with the density of levels of p-symmetry, according to calculations ([1])), is capable of reflecting the distribution of 3d-like states in the hybridized dsp-energy band of a metallic crystal ([2–4]). In other works ([5]) it is considered that this line owes its origin predominantly to electronic transitions from 4p-states, while the contribution of 3d-states is negligible. A compromise concept was expressed in ([6]): the shape of the K_{β_5}-band reflects the form of the distribution of 3d-like states, while its absolute intensity is due mainly to an admixture of p-states in the hybridized dsp-band.

In the behavior of the K_{β_5} line of 3d-metals, in the systematics of spectra attributed to the quadrupole transition 3d—1s ([2]), two peculiarities are observed experimentally: the line has an enhanced intensity, unusual for quadrupole lines (the admixture of states of p-symmetry in the external dsp-band is relatively small in this case), and its intensity passes through a maximum at $Z = 24 \div 26$ ([2]). For a qualitative explanation of the increased brightness of the line, a number of works ([2–4]) use a model of induced dipole transitions caused by the involvement of 3d-electrons in chemical bonding. However, the existence of the K_{β_5} line in Zn and As vapors ([7]) indicates that this explanation is not exhaustive. The second peculiarity of the behavior of the K_{β_5} line—the anomalous course of the intensity—has not received a satisfactory explanation up to now, although the fact that the intensity maximum of the K_{β_5} line falls on the elements with the largest spin moment in the 3d-shell ($Z = 24 \div 26$) points to a possible connection between these phenomena, by analogy with a similar

connection established for a number of characteristics of the dipole lines of the same series. Below an attempt is made to estimate the share of quadrupole transitions (the fundamental possibility was proved in [1]) in the excitation mechanism of the K_{β_5} line, and also to use the quadrupole approximation to explain the nonmonotonic behavior of its intensity with increasing Z.

It is known that the probability of quadrupole transitions in the x-ray region of the spectrum is greater than in the optical region [8,9] and increases with increasing Z. A rough estimate of the lifetimes of dipole and quadrupole transitions, for example, in hydrogen-like atoms leads to the relation

$$\tau(3d-1s) \sim \tau(3p-1s)(137/Z)^2 \cdot {}^1/_5. \tag{1}$$

A more accurate estimate requires calculation of the matrix elements D and Q in the formulas for the probabilities of dipole and quadrupole transitions

$$A_d = \frac{64\pi^4}{3hc^3}\nu^3 D^2, \tag{2}$$

$$A_q = \frac{32\pi^6}{5hc^5}\nu^5 Q^2. \tag{3}$$

Taking in (2) and (3) $\nu = 3{\cdot}10^{18}$, which corresponds to $\lambda = 1$ Å, and substituting the numerical values, we obtain

$$A_q/A_d = 3 \cdot 10^{15}|Q/D|^2. \tag{4}$$

Calculation of D and Q for the transitions $3p$—$1s$ and $3d$—$1s$ with self-consistent-field wave functions for free atoms of the $3d$-metals [10] gives

$$|Q/D|^2 \approx 1.3 \cdot 10^{-19},$$

and finally

$$A_q/A_d \approx 4 \cdot 10^{-4}. \tag{5}$$

For the optical region of the spectrum this ratio is smaller by several orders of magnitude.

The theoretical ratio of the intensities of the K_{β_5} and K_{β_1} lines, which can be obtained from (5), owing to differences in the selection rules for dipole and quadrupole transitions and in the numbers of final hole states allowed by the Pauli principle, increases by 1—$1\frac{1}{2}$ orders of magnitude. Experiment for the

ratio of the intensities of the K_{β_5} and K_{β_1} lines gives values lying in the range $3 \cdot 10^{-2} \div 5 \cdot 10^{-3}$ [(2)].

The closeness in order of magnitude of the calculated (in the quadrupole approximation for K_{β_5}) and experimental values of the intensity ratio of the K_{β_5} and K_{β_1} lines indicates the significance of the contribution of quadrupole transitions and the advisability of further approximations connected, in particular, with refinement of the wave functions.

Analysis of the matrix elements $\int R(1s)r^2R(3d)\,d\tau$ for $3d$-metals shows that the largest contribution to them is obtained at values $r = (0.15 \div 0.4)a_0$, whence it follows that, in a semiclassical treatment [(11)], the size of the radiating system is ~ 0.2 Å. This value is commensurate with the wavelength (1 Å) of the radiation, which accounts for the slow convergence of the expansion of the retarded potential and the inapplicability in the present case of the dipole approximation, obtained for $\lambda \gg a_0$.

Let us consider in more detail the systematics of transitions between the shells $1s^1$ and $3d^x$ $(x \leq 10)$. Formation of a vacancy in the shell $1s^2$ gives the term ^2S. The terms of the shell d^x, allowed by the Pauli principle, are given in Table 1 [(11)]. In accordance with the selection rules in J for quadrupole transitions $(\Delta J = 0, \pm 1, \pm 2)$, in the LS-approximation combinations are possible only between the shells $1s^1$ and $3d^x$ with odd x, since for even x half-integer ΔJ are obtained. However, in the behavior of the K_{β_5} line no anomalies are observed experimentally for even x, which testifies to the identity of the mechanisms of the K_{β_5} line for all x. These circumstances give grounds to assume that in the initial excited state of the atoms there takes place interaction between the configurations $1s^1$ and $3d^x$, leading to a change of the total angular momentum. In an analogous manner, in [(8)] the existence and multiplet character of the α and β lines of the M-series of rare-earth elements were explained.

Because of the remoteness of the $1s$- and $3d$-shells, we shall consider the $1s^1$—$3d^x$ interaction in the jj-scheme. In this case the selection rules in J will be applied to the configurations $1s^2 \ldots 3d^{x-1}$ (final) and $1s^1 \ldots 3d^x$ (initial).

The $1s\,3d$-interaction, although small in magnitude, will lead to the formation of new levels with $J' = J \pm 1/2$ (Table 2), which will ensure fulfillment of the selection rules in J. A comparison of Tables 1 and 2 then shows that the selection rule $\Delta J = 0, \pm 1, \pm 2$ is fulfilled for transitions between the configurations $1s^1 \ldots 3d^x$ and $1s^2 \ldots 3d^{x-1}$ for any x.

The number of combinations ensuring fulfillment of the selection rules $\Delta J = 0, \pm 1, \pm 2$ between the configurations $1s^1 \ldots 3d^x$ and $1s^2 \ldots 3d^{x-1}$ is not constant, but depends on x.

Table 1

Terms of the d^x shell permitted by the Pauli principle

x	Terms	$\lvert L-S\rvert \leq J \leq\leq \lvert L+S\rvert$
1, 9	^2D	3/2, 2/5
2, 8	$^1S\,DG\ \ ^3PF$	0 to 4
3, 7	$^2PDFGH\ \ ^4PF$	1/2 to 11/2
4, 6	$^1SDFGI\ \ ^3PDFGH\ \ ^5D$	0 to 6
5	$^2SPDFGHI\ \ ^4PDFG\ \ ^6S$	1/2 to 13/2

A concrete calculation shows that for Ti this number is 9, for V 22, for Mn 31, for Fe 29, and then decreases, i.e., the dependence of the number of combining levels passes through a maximum located at $Z = 24 \div 26$. If it is assumed that transitions between any pair of combining levels are equally probable, then, in order to obtain the ratio of the intensities of the $3d-1s$ and $3p-1s$ transitions for different Z, the quantity (5) should be multiplied by numbers greater than 1 and proportional to the numbers of allowed combinations for each x. This leads to the above-mentioned increase of the ratio (5) and to a nonmonotonic dependence of this ratio on Z.

Thus, inclusion in the mechanism of the K_{β_5} line of quadrupole $3d-1s$ transitions, the significance of whose contribution is confirmed by direct calculations of the corresponding matrix elements, makes it possible to establish a connection between the spin moment of the atom and the intensity of K_{β_5}.

Table 2

x	1, 9	2, 8	3, 7	4, 6	5
$J' = J \pm 1/2$	1-3	1/2-9/2	0-6	1/2-13/2	0-7

Such a connection is observed not only in going from one element to another, but also for a single element occurring in compounds where, according to the ionic model, different spin moments in the $3d$-shell of this element may be assumed. Table 3 gives experimental results of measurements of IK_{β_5} from ions of different valence of certain $3d$-elements in an oxygen environment. As the spin moment of the ion increases, a noticeable increase in the intensity of the K_{β_5} line is observed.

Recently performed self-consistent-field calculations of the band structure of Ti in a number of binary compounds of metallic type [14] and in the homogeneity range of TiC [15], as well as of pure copper [16], demonstrated a great similarity between the theoretical and experimental K_{β_5}-bands [17] in shape, width, and position on the energy scale, especially in the region adjacent to the Fermi level. At the same time, the statistical weight of $3d$-states in the band proved to be large, while that of $4p$-states, on the contrary, was very small. Moreover, as shown in [15], the symmetry of the $3d$-wave functions, which clearly divides

them into two groups, one of which (d_{z^2, x^2-y^2}) has the same angular distribution in K-space as the p-wave functions, plays an important role in the formation of the band density. This circumstance, although not taken into account in our calculations, cannot fail to affect the transition probability in the aspect under discussion (the contribution of $3d$-states to the intensity K_{β_5}).

It should be noted that for $4d - 1s$ transitions no dependence of the intensity of the corresponding line on atomic number analogous to ···

that for the K_{β_5} line. This circumstance, however, does not call into question the model of quadrupole transitions applied above to K_{β_5}, for the following reason. The matrix elements $\left|(1s|r^2|4d)\right|$ must be much smaller than the matrix elements $\left|(1s|r^2|3d)\right|$, which, first, will reduce the probability of the $4d$—$1s$ transition and, second, will reduce the $1s^1 4d^x$ interaction that leads to a violation of the selection rules. Moreover, what is very essential, the filling of the $4d$-shell with electrons occurs differently from that of the $3d$-shell. This is indicated, in particular, by differences in the x-ray spectra of $3d$- and $4d$-metals ([18]).

Table 3

Intensity of the K_{β_5} line from $3d$-metals in compounds

Compound	Configuration of the $3d$-metal ion in a purely ionic model	Intensity of the K_{β_5} line, arbitrary units	Source
Cr metal	$3d^5 4s^1$	1	([12])
Cr_2O_3	$3d^3 4s^0$	0.7	([12])
K_2CrO_4	$3d^0 4s^0$	less than that of Cr_2O_3*	([12])
$SrCrO_4$	$3d^0 4s^0$	less than that of Cr_2O_3*	([12])
Mn_3O_4	$3d^{4,3} 4s^0$	0.80 ± 0.02	([13])
MnO_2	$3d^3 4s^0$	0.69 ± 0.02	([13])
Fe_3O_4	$3d^{4,7} 4s^0$	51 ± 2.5	From the authors' experiments.
Fe_2O_3	$3d^5 4s^0$	56 ± 2.5	From the authors' experiments.

* Numerical characteristics are not given.

Thus, the entire set of observations concerning the fine structure of the x-ray K-spectra of $3d$-metals, the calculations and theoretical considerations presented above, as well as the data of recent quantum-mechanical calculations of densities

of states of various symmetries in the band structure, testify in favor of the idea that quadrupole $1s$—$3d$ transitions make a substantial contribution to the intensity and shape of the K_{β_5} line of $3d$-metals and their compounds.

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Received
10 I 1968

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Note: Figure translations are in progress. See original paper for figures.