The Energy Level of the Valence Electron in Cu, Viewed from Its X-Ray Spectrum (II, 1)

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Mitsuru SATÔ

The Research Institute for Iron, Steel and Other Metals

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Synopsis

A method of investigation which may be appropriately called the "synthetic method" is proposed; in this method the behaviour of the valence electron in a metal is not assumed from the starting of investigation, as usually done in the prevailing theory of metals; but, from X-ray spectrum, the energy level or levels which are expected to be associated by the valence electron, are determined. For Cu, it was taken as that, X-ray L-satellites, $L\beta'$, λ 12.989, β''' 12.911; α'' 13.233, α'''' 13.176Å, [E. Gwinner, Zeits. Phys. 108 (1938), 523], are due to the transitions, L_{II}-E_1, L_{II}-E_3; L_{III}-E_2, L_{III}-E_4, respectively, $E_1 \sim E_4$ being the energy levels associated by the valence electron; next, they were combined with K_{α_2} and K_{α_1}, respectively, and obtained the distances from K; finally the relative positions of $E_1 \sim E_4$ were computed for comparison with the other phenomena which are expected as due to the behaviour of the same electron as above concerned, this comparison being done in the next paper.

I. Introduction

We believe that, most properties of metals have their ultimate origin in the behaviours of the valence electrons in them. So, for the establishment of the electron theory of metals, satisfactorily, it is important to determine the energy state of the valence electron in metals, conclusively. In the prevailing theory, however, a model is generally accepted as the starting point of investigation; and one endevours to explain the properties of metals and the phenomena in them, deductively. The investigation along this line, has been carried out, long, by many authorities, the main results being mentioned in the books referred to bellow(1); but in spite of such efforts, many evidences which are very important, in theory or practice, such as supraconduction or the transformations of iron, are not yet explained, satisfactorily, from the view point, as above stated. So, we turned to think that, the "deductive method" of investigation as above stated, is not suitable for the complicated subject as metals, and further that, the

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* The 574th report of the Research Institute for Iron, Steel and Other Metals. The results of the present series of investigations have been hitherto reported under the general title, "On the Energy State of the Valency Electrons in Some Metals", but hereafter, this will be omitted, and only with the subtitle, with the numbering such as (I, 18) for Zn, and (II, 1) for Cu, will be published.

(1) L. Brillouin, Die Quantenstatistik (1931); A. Sommerfeld, H. Bethe, Handbuch d. Physik 24/2 Kap. III. (1933); N. F. Mott, H. Jones, The Theory of the Properties of Metals and Alloys (1936); H. Frölich, Electronen Theorie d. Mettalle (1936); F. Seitz, The Modern Theory of Solids (1940).

"synthetic method" may be prefable to the former. It means that, since various properties of a metal and many phenomena in it, come from the same source, i. e., the behaviours of the valence electron in the metal, so, if we avail these evidences, and trace backward to their common origin, it may be possible to ascertain the real phase of the valence electron, at least, in this metal. Furthermore, if we can select a phenomenon in which the elementary process of the valence electron reveals most evidently, then the above method may be applied in an effective way as follows:— First, from the above phenomenon we determine the energy level, associated by the valence electron, in question, though it may happen to be provisional. Next, another phenomenon in the same metal, relating most intimately with the former, is selected, and with the aid of this, the above result of investigation is confirmed, corrected or refined to be more perfect. Thus the investigation is extended, by and by, from one phenomenon to another, of course most of them are concerned to the above metal, and the result of investigation is improved, step by step; and when all evidences which are available, are exausted, then, we think, it is possible to determine the above energy state, most reliably, and the evidences, above treated, may be explained, in a unified way, as due to the behaviours of the valence electron, under consideration. Further, when the above method of investigation is extended to other metals and alloys, in the same way as above described, always improving the former conclusions, then, we think, it is possible to establish the electron theory of metals which would be more perfect than the prevailing, at present.

In order to undertake the above plan, however, it must be most important that, which phenomenon is to be first selected as the starting point. But this problem is answered clearly by the history of the development of the atom physics; namely, the elementary process of the electron, under consideration, reveals most evidently, in the interaction between the electron and radiation; for the present case, expectably, in the X-ray spectrum with which the valence electron associates. Accordingly, the observation and the analysis of the above spectrum is the first task in our investigation.

In the program as above stated, the present writer carried out a series of investigations on Zn,[2] since 1936, and, though some of them must be revised or improved with the progress of investigation, it may be said that, the first survey of investigation on Zn is finished. So, the next study is on Cu, and the present report is the first.

II. Analysis of L-satellite-lines of Cu-X-ray

As the X-ray spectrum which will be treated with the purpose as above stated,

(2) M. Satô, Sci. Rep. Honda Anniv. Vol. (1936), 136; 25 (1936), 197; 25 (1936), 771; 25 (1937), 829; 25 (1937), 871; 26 (1937), 206; 26 (1937), 341; 26 (1937), 377; 27 (1938), 137; 27 (1939), 278; 28 (1939), 143; 28 (1940), 398; 29 (1940), 87; 30 (1942), 137; 30 (1942), 267; 31 (1942) 38; 31 (1943), 153; 31 (1943), 157; 31 (1943), 163; Sci. Rep. RITU. 1 (1949), 51.

the L-emission lines are most suitable in the case of Cu. These lines have been already measured by several workers as shown in Table 1.

Table 1. L-Emission lines of Cu-X-ray.

Siegbahn and Thoraeus[3] (1924)		Thoraeus[4] (1926)		Karlson[5] (1930)		Saur[6] (1936)		Gwinner[7] (1938)	
				β''	12.90Å			β'''	12.911Å
β''	12.96Å	β''	12.96Å	β'	12.96	β''	12.97Å	β''	12.957
β'	12.97	β'	12.99			β'	13.00	β'	12.989
$L\beta_1$	13.027	$L\beta_1$	13.029	$L\beta_1$	13.027	$L\beta_1$	13.03	$L\beta_1$	13.026
α''	13.17	α''	13.172	α''	13.19	α''	13.17	α''''	13.176
α'	13.24	α'	13.24	α'	13.23	α'	13.25	α''	13.233
								α'''	13.261
						K comp.	13.29	α'	13.277
$L\alpha_{1,2}$	13.31	$L\alpha_{1,2}$	13.308	$L\alpha_{1,2}$	13.306	$L\alpha_{1,2}$	13.31	$L\alpha_{1,2}$	13.301
								α^{V}	13.372
								α^{VI}	13.397

From this table it is seen that, Gwinner's result seems most reliable, and so, this will be taken as the starting of the investigation as above described.

Now as generally accepted, $L_{\alpha_{1,2}}$ and L_{β_1} are generated from the electron transitions, L_{III}-$M_{IV,V}$ and L_{II}-M_{IV}, respectively. Hence, the wave-lengths of the lines which are emitted by the transitions between the valence electron level and L_{III}, L_{II}, if they exist, must be shorter than those of $L_{\alpha_{1,2}}$, L_{β_1}, respectively. Hence the Gwinner's lines, $\alpha'\sim\alpha''''$ and $\beta'\sim\beta'''$ satisfy the above condition. So, at first, we took all of them, provisionally, as those of the above nature, and compared them with the photoelectric effect of Cu, the spectrum of light absorption by its thin film, and others, these phenomena being considered to be in most intimate relation with the above X-ray spectrum. Thus, after many trials, we reached the conclusion that, $L\beta'\lambda$ 12.989, β''' 12.911, α'' 13.233, α'''' 13.176Å, are the lines, we are searching for, and the others are not; saying more in details, though the latters may be associated by the valence electron, indirectly, but are not generated by the transitions from the stationary state of the above electron. The above procedure, however, was carried out in zigzag way, and accordingly, it is too complicate to be described here in detail. So, for simplicity, we assume here the above conclusion as correct, and the stationary level, associated by the valence electron, will be determined, provisionally, in the next section.

(3) M. Siegbahn, R. Thoraeus, Ark. Mat., Astr. o. Fys. 18, 24, 6 (1924).
(4) R. Thoraeus, Phil. Mag. (7) 2, 1007 (1926).
(5) A. Karlson, Ark. Mat. Astr. o. Fys. (A) 22 Nr. 9 (1930).
(6) E. Saur, Zeits. Phys. 103 (1936), 421.
(7) E. Gwinner, Zeits, Phys. 108 (1938), 523.

III. Determination of the energy level of the valence electron in Cu

On the basis of the conception as above stated, the lines $L\beta'$, β''', α'' and α'''' are taken as due to the transitions, as shown in Table 2, where E_1, E_2, E_3 and E_4 denote the energy levels, associated by the valence electron, the sufix being attached to be in the order of the energy position, as illustrated in Fig. 1.

Table 2. Transitions of valence electron.

Line	λ (Å)	ν/R*	Transition
$L\beta'$	12.989	70.157	L_{II}-E_1
$L\beta'''$	12.911	70.581	L_{II}-E_3
$L\alpha''$	13.233	68.863	L_{III}-E_2
$L\alpha''''$	13.176	69.161	L_{III}-E_4

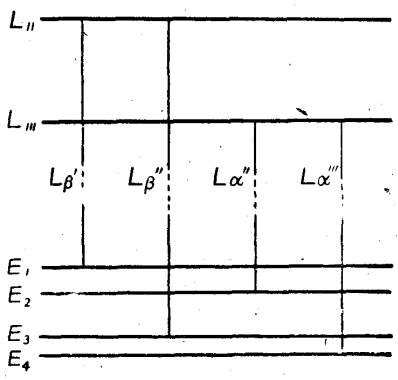

Fig. 1.** Diagram, illustrating the energy levels of valence electrons.

Next, the energy distances of $E_1 \sim E_4$ from K will be computed by combinations, for which $K\alpha_1$, $K\alpha_2$ are necessary; they were measured very accurately as shown in Table 3. From Tables 2, 3, the energy distances, under consideration, were obtained as shown in Table 4.

Table 3. Accurate values of Cu $K\alpha_1$, $K\alpha_2$ (X-unit).

	$K\alpha_1(K\text{-}L_{III})$	$K\alpha_2(K\text{-}L_{II})$
Siegbahn(8)	1537.396	1541.243
Wennerlöf(9)	1537.395	1541.232
Bearden, Shaw(10)	1537.400	1541.220
Mean	1537.397	1541.232
ν/R	592.733	591.258

Tadle 4. Energy distances of $E_1 \sim E_4$ from K.

	$K\text{-}E_1$	$K\text{-}E_2$	$K\text{-}E_3$	$K\text{-}E_4$
ν/R	661.415	661.596	661.839	661.894

Table 5. Relative positions of $E_1 \sim E_4$.

	ν/R	eV	λ (Å)
E_1-E_2	0.181	2.46	5030
E_1-E_3	0.424	5.76	2150
E_1-E_4	0.479	6.50	1900
E_2-E_3	0.243	3.00	3750
E_2-E_4	0.298	4.05	3036
E_3-E_4	0.055	0.75	16600

Further, for the later use, the relative positions of $E_1 \sim E_4$ were computed as shown in Table 5.

Now, as above stated, if these results are correct, various properties and phenomena which are due to the valence electron, must be explained from the above results, or be at least, in harmony with them. So, in the next paper, the comparison with the intimate phenomena as above stated, will be done with the

* Throughout this paper and the ones to continue, the value of R, $R_\infty = 109{,}737.50$ is used.

(8) M. Siegbahn, Ark. Astr. o. Fys. (A) 21 Nr. 21 (1929).

(9) I. Wennerlöf, Ark. Mat., Astr. o. Fys. (A) 22 Nr. 8 (1930).

(10) J. A. Bearden, C. H. Shaw, Phys. Rev. 48 (1935), 18.

** $L\beta''$ and $L\alpha'''$ are to be corrected as $L\beta'''$ and $L\alpha''''$, respectively.

aim, as already described above. Concering the lines which are excluded above, an attempt will be made to explain them in an appropriate opportunity, in a later paper.

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