Identification of the two-electron one-photon transition in Eu III in electron-atom collisions

V. L. Goldovskiĭ, L. L. Shimon, I. P. Zapesochnyĭ, and A. M. Solomon
Uzhgorod State University

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The formation of a double $5p$ vacancy in an europium atom and the emission of a single photon ($\lambda = 68.3$ nm) in the course of filling this vacancy by $5s$-and $6s$-subshell electrons is first identified.

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In this work we report on experiments in the excitation of outer closed atomic shells of rare-earth elements by electron shock. The nature of excitation of the $5p$-subshell electrons of a series of rare earths (Sm, Eu, Tm, Yb) was studied from the vacuum ultraviolet (VUV) spectra. This paper deals with experimental identification and the analysis of single-photon emission due to filling of a double vacancy in the $5p$-subshell of europium by electrons from different shells.

The experimental setup,[1] involving crossed electron and atomic beams, was used to investigate the emission spectrum of europium in the VUV region (40-140 nm) generated at different energies of bombarding electrons. As evidenced, the majority of closely-space line groups in these spectra share a common excitation threshold ~ 30 eV and occur as a result of filling of vacancies in the $5p$-subshell generated in the course of electron-atom collisions.[2]

The comparatively high effectiveness of $5p$-subshell ionization by electron shock[2] depends solely on the stability of the half-filled $4f$ subshell[3] that screens the $5p$ subshell from the nucleus. This circumstance provides the basis for assuming that the europium $5p$ subshell has an appreciable degree of probability of being doubly ionized.

An unidentified group of lines in the Eu spectrum with wavelength $\lambda = 68.3$ nm (see Fig. 1) was used as raw data. Additional experiments yielded a distribution function for this group (see Fig. 2) and helped determine its excitation energy (~ 75 eV).

The aforementioned line group occurring at such a high potential may be inter-

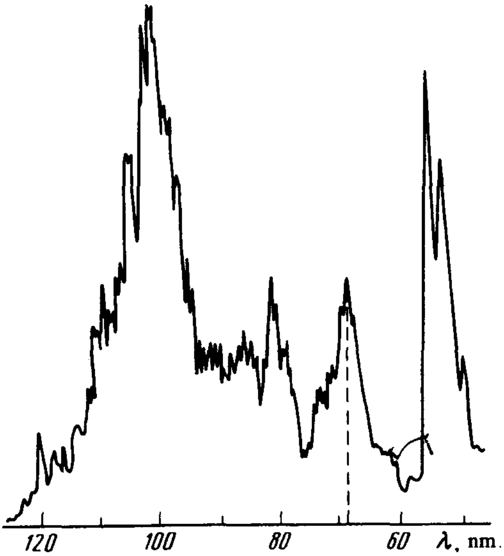

FIG. 1. Spectrum of europium atom for bombarding electron energy of 150 eV.

preted as a consequence of either radiative transition between the excited state of triple Eu IV ion or radioactive decay of a double $5p$ vacancy. However, the first process is associated with considerable rearrangement of electron shells as a result of the escape of both outer $6s$-electrons, one $4f$ electron and, furthermore, the excitation of one of the surplus electrons to the nonresonant nl-state. The more likely process, however, consists of the removal of only two electrons from the well-shielded $5p$ subshell, without affecting the stable $4f$ europium sublattice.

Evidently, reliable identification of the subject line group ($\lambda = 68.3$ nm) calls for knowing the energy required to form a double $5p$-vacancy in an Eu atom. In the solution of similar problems calculations are normally based on the quantum theory of many-body problems and are aided by an electronic computer.[4] However, these calculations are complex and laborious, particularly for multi-electron atoms. It is, therefore, expedient to obtain at least an estimated value of energy required to form the double vacancy in an atom, assuming some model for the latter.

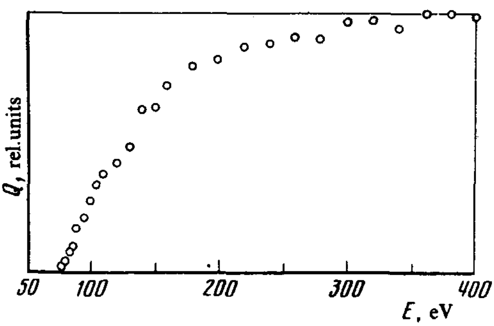

FIG. 2. Energy dependence of radiation intensity of europium in the region $\lambda = 68.3$ nm.

With this in mind, we picked the spherically-symmetric atomic model in which electron charges appear to be uniformly distributed over the surface of spheres with radii r calculated by means of the Hartree-Fock-Slater method for the corresponding subshells with the quantum numbers n and l[5] It may be assumed that the energy required to form a vacancy $E^{2+}(r)$ equals twice the energy required to form a single vacancy $E^{+}(r)$ plus a certain energy surplus:

$$E^{++}(r) = 2E^{+}(r) + \Delta E(r), \tag{1}$$

The energy supplement depends, in a general case,[4] on the following: (1) redistribution of electron shells during ionization of atom, (2) interaction between vacancies, (3) virtual excitation of other vacancies. Expressions for $E^{2+}(r)$ and $E^{+}(r)$, obtained on the basis of the selected atomic model, yield a simple formula for the energy supplement:

$$\Delta E(r) = e^2/r, \tag{2}$$

where e is electron charge.

The table below shows double-ionization energies of certain Group III elements which we calculated assuming the spherically-symmetrical electrostatic model of the atom. Also shown for comparative purposes are experimental data.[6] On the whole, as the tabulated data show, results of our calculations agree well with the experiment; this was used as a criterion for using such an atomic model for estimating the energy required to form a double $5p$-vacancy in an Eu atom. This energy, according to our calculations, is 75 eV, a value which is in good agreement with the experimentally-determined threshold excitation energy of the group of spectral lines $\lambda = 68.3$ nm (see Fig. 2).

TABLE I.

Element	Configuration of Basic Atomic State	Configuration of Basic Doubly Ionized Ion	E^{++}, eV calculation	E^{++}, eV experim. [6]
Al	$2p^63s^23p$	$2p^63s$	23.88	24.81
Sc	$3p^63d4s^2$	$3p^63d$	19.52	19.45
Ga	$3d^{10}4s^24p$	$3d^{10}4s$	24.38	26.51
Y	$4p^64d5s^2$	$4p^64d$	18.99	18.61
In	$4d^{10}5s^25p$	$4d^{10}5s$	22.68	24.64
La	$5s^25d6s^2$	$5s^25d$	16.46	17.04
Tl	$5d^{10}6s^26p$	$5d^{10}6s$	26.09	26.53
Eu	$5p^64f^26s^2$	$5p^64f^7$	16.93	16.91
Yb	$5p^64f^{14}6s^2$	$5p^64f^{14}$	29.59	29.20

To identify the lower state of Eu III which corresponds to the observed emission at $\lambda = 68.3$ nm (photon energy 18 eV), we calculated the energies of different electron configurations based on the proposed model since the available data[7] were incomplete. Detailed analysis showed that the lower state for $\lambda = 68.3$ nm is best matched by the $5s5p^6 4f^7 6s$ configuration for which the calculated energy is 56.43 eV.

Thus, the occurrence of a line group with $\lambda = 68.3$ nm in the VUV spectrum of europium may be interpreted as the consequence of a one-photon two-electron transition, i.e., radiative decay of a double $5p$-vacancy formed in a single collision of an electron and europium atom as follows:

$$\begin{array}{l} \mathrm{EuI}\ (5s^2 5p^6 4f^7 6s^2) + \mathbf{e} \rightarrow \mathrm{EuIII}\ (5s^2 5p^4 4f^7 6s^2) + 3e \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad\qquad\qquad \mathrm{EuIII}\ (5s\,5p^6 4f^7 6s) + h\nu \end{array} \qquad (3)$$

where $\mathbf{e}$ is the bombarding electron and $h\nu$ is observed emission photon.

We should note that the above radiative transition is forbidden by the selection rules in the presence of LS coupling. However, assuming an LS coupling when considering processes occurring in the inner atomic shells fails to yield satisfactory results, especially for such complex systems as the europium atom.

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