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Correlation effects in double-K-vacancy production

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The probability of double-K-vacancy production accompanying internal conversion in three different atoms. In ($Z = 49$), Ba ($Z = 56$), and Tl ($Z = 81$) has been measured in coincidence experiments. The comparison of our experimental results with various theoretical approaches exhibits the importance of correlation effects between the two K electrons.

I. INTRODUCTION

The creation of multiple vacancies in atoms strongly depends on the mode of interaction and can provide useful information on the collision mechanisms as well as on the atomic structure. When using heavy-ion bombardment, for instance, which introduces in the atom a very strong perturbation, the single-vacancy production is so large that the probability of double vacancy is simply equal, at first order, to the square of the probability of single-vacancy production. In such a case both electrons can be considered as completely independent in the central-field approximation. When the ionizing agent introduces a very weak perturbation in the atomic cloud, like in the electron bombardment, photoionization, internal conversion or nuclear electron capture, the probability of single-vacancy production is very low and the instantaneous correlation effects between both electrons may play an important role and have to be taken into consideration (one electron is "pushing" the other). In this case one has to consider in the most general way the interaction of the impinging particle with the two considered electrons and at the same time the relative interaction between these two electrons (one then neglects the influence of all the other electrons in the atom). In this paper we present some results we have obtained about the double-K-vacancy production in various atoms during internal-conversion process. The double-K-vacancy production is, in such an interaction, very sensitive to Coulomb-correlation effects that we will discuss in comparing our experimental results with various theoretical approaches.

II. THEORY

It was found a long time ago, that for very weak interactions in which the probability of a single ionization P_i is very low, the experimental probability for double ionizations in shell i and j is much higher than it can be predicted in considering both electrons as completely independent, i.e., when the probability for double ionization is equal to $P_i \cdot P_j$ (i.e., very small and sometimes negligible). These results clearly exhibit the effect of the interaction between the two considered electrons during the collision. The first effect of this electron interaction that has been taken into consideration is the relaxation of the atomic orbitals during the ionizing event. It was pointed out in 1941 by Migdal and Feinberg[1,2] that during the relaxation of the atomic orbitals accompanying the change of the nuclear charge in β decay there is a quite large probability of ionization in each of the atomic inner levels. This effect obviously has to play a role in any process in which there is a change of the inner screening and can explain at least partly the intensity of multi-ionization processes observed in electron bombardment, photoionization, and internal conversion.... This model in which all the electrons relax independently of one another (i.e., not taking into account correlation effects) has been first successfully used by Carlson, Krause, and Åberg[3-6] to explain the double ionization probability during electron bombardment and photoionization. This so-called shake model is now commonly used and leads to a good agreement, at first order, with experiments when considering double ionization in different shells. When considering double ionization in the same shell, or very precise experiments of double ionization in different shells, one cannot simply consider that the orbitals may relax independently of one another and one has to take into account correlation effects. The simplest case of double ionization (or excitation) of two electrons coming from the same shell is the one of helium and has extensively been studied in the past fifteen years. Recently Schmidt *et al.* have carefully measured this double-ionization cross section in the case of electron bombardment[7] and that of photoionization[8]. The very high probability of this double-ionization process with respect to that of single ionization, that may attain in the asymptotic limit 4%, clearly exhibits how important may be the correlation effects between the two considered electrons.

The most general and powerful method to de-

scribe the atomic correlation effects is the many-body perturbation theory. This method which leads in general to a very good agreement with experimental results is however very difficult and no calculation has yet been carried out in the case of double ionization in the K shell of a many-electron atom. An alternative method to describe these correlation effects in a simpler way, is the generalized sudden approximation of Åberg[6] that we shall use to interpret our results.

In this method only the two K electrons are taken into consideration, the effects of all the other ones being rejected in the central field. The principle of this method is to use the general formalism of the shake model, that can be generalized as demonstrated by Åberg (generalized sudden approximation) and to make use of parametrized effective wave functions like those used by Hylleraas[9] which take into account the correaltion effects, instead of the Hartree-Fock wave functions. One calculates the probability that during a K ionization the second K electron will remain with its own quantum number, i.e., $|\langle\Psi_K^f|\Psi_K^i\rangle|^2$ (using correlated wave functions) where Ψ_K^i and Ψ_K^f are, respectively, the wave function of $(1s)$ electron in initial and final states. In this method however, correlation between the two electrons in the final state (in continuum or excited bound states) is not taken into account. In a heliumlike atom there are two different kinds of final states: "shake-off states" in which the two electrons are ejected into the continuum and "shake-up states" in which one electron is ejected into the continuum, the second one being promoted into a nonoccupied excited state. When studying many electron atoms like thallium for instance, most of the shake-up processes are precluded, most of the lowest excited states being occupied. In the calculations using the heliumlike approximation, one then needs to calculate separately, still using correlated wave function in the initial state, the contribution of this effect that has to be withdrawn. The purpose of our work is to study a few elements over a large range of Z values for the effect of the correlated movement of two K electrons as predicted by Åberg.[6,10]

III. EXPERIMENTAL METHODS AND RESULTS

In any of the cases of interest (weak perturbations) the probability of double-K-vacancy production is very low and difficult to measure accurately. The detection of double-K ionizations can be achieved either looking at the ejected electrons or at the characteristic rays following the atomic rearrangement. The most accurate way to measure the relative double-K-vacancy production (P_{KK}/P_K) is the study of the intensity of the K-hypersatellite lines relative to that of the diagram lines assuming, which seems to be well supported by calculations[11] a constant fluorescence yield. This method is so far, in any case, much easier and more accurate than the absolute measurement of the total number of electrons in a continuous spectrum. There are two possibilities for detection of the hypersatellite lines that have both been used successfully: The direct observation of the lines with a crystal spectrometer[12-15] and the coincidence method[16]. The crystal spectrometry method that has only been recently carried out needs very strong sources or very long exposures considering the very low transmission of this device (10^{-8} typically). It has mainly been used except in a few cases[15] to study light elements. The second method is by the identification, in a coincidence experiment, of the cascade $K^{-2}\rightarrow K^{-1}L^{-1}$ (K_α^h hypersatellites) $-K^{-1}L^{-1}\rightarrow L^{-2}$ (K_α satellites) and has been used with radioactive samples only, for light as well as for heavy elements. One needs two solid-state detectors, taking into account the maximum admissible counting rate compatible with good resolution, and best true to random coincidence ratio. Even with this requirement met, one still needs very long exposure, and very high instrumental stability.

Most of the weak atomic perturbations that can provide information about inner-shell correlation effects (electron bombardment, photoionization, and internal conversion of a γ ray) lead to the same asymptotic P_{KK}/P_K value and we can choose the mode of excitation on an experimental basis. Electron bombardment which is the most usual mode of excitation in x-ray spectroscopy is very difficult to use taking account of the very intense bremsstralhung that appears with high-Z targets and hides the weak hypersatellite lines. Photoionization, which would appear at first glance, the best mode of excitation is also still difficult to use, the present available photon beam being not intense enough (even when using synchrotron radiation) to get spectra in a reasonable time of exposure. The internal conversion that provides inner-shell ionizations as a consequence of nuclear de-excitation is, from a theoretical point of view, identical to the photoionization process (virtual photoionization) and seems, at present time, to be the most convenient mode of production of double-K vacancies. We have then chosen to use the coincidence method with radioactive samples decaying by the internal-conversion processes.

We have studied the K-hypersatellite spectrum of In, Ba, and Tl accompanying K internal conversion. In the case of In we have studied two

isotopes in order to test if there is any influence of the transition (energy and multipolarity) on double-K ionization. ^{113}In and ^{114}In which have a long half-life isomeric state, are directly studied from In sources. ^{137}Ba and ^{203}Tl are observed following the β decay of ^{137}Cs and ^{203}Hg. The different decay schemes are shown Table I.

^{114}In, ^{137}Cs, and ^{203}Hg are β emiters. In order to prevent the detection of electrons, plexiglass foils of 1-mm thick were placed on either side of the source. These sources have a long half-life so, it has been possible to record the XK spectrum continuously during runs of 3 to 5 weeks. For ^{113}In the half-life of which is only 100 min., we have performed 150 successive 100 min. runs. ^{113}In was obtained by repetitive elution from its parent ^{113}Sn fixed on an ion-exchange resin. After adequate dilution to reach a given specific activity one drop of In solution was evaporated on a thin plexiglass disc. The whole operation took no more than 5 min. With this method ^{113}Sn contamination was very small and its spectrum does not interfere with that of In K hypersatellite. In all cases the sample activity was approximately 1 μCi. This intensity is the result of a compromise between the highest intensity (for high statistic) and the best true to random coincidence ratio. The diagram and hypersatellite K lines of the considered elements were detected with two high-resolution solid-state detectors (SiLi or GeLi according to the energy range) in a biparametric setup. Then in the same exposure it was possible to resolve the part of the true and random coincidence[17]. The energies of the hypersatellite lines that have been previously studied[16] are presented in Table II.

We present in Fig. 1 the XK-XK coincidence spectrum obtained following the internal conversion in ^{113}In. The detector resolution does not allow one to resolve the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines except in the case of Tl. The K_α^h line is very well resolved from the K_α line but K_β^h cannot be observed because it overlaps with the K_β spectrum.

The K_α^h/K_α ratio obtained in our experiments is presented Table III. These results take into account the statistical fluctuation and the incertitude introduced by the K_α^h line deconvolution. For the lightest elements (In, Ba) the K_α^h/K_α ratio does not correspond exactly to the P_{KK}/P_K ratio, since the $K_{\alpha_1}^h$ transition is partially forbidden for these elements[22]. In Table III we have compared our experimental data with those obtained recently by other authors. In the case of thallium, for which we have made several experiments, our value is definitely smaller (by a factor of 2) than the only reported one.[21] Furthermore, using two different methods of extraction of the data, either the absolute method that needs the knowledge of the absolute solid angle and efficiency of detectors, or the relative method based on the ratio of true to random coincidence we have always obtained consistent results. Finally using

TABLE I. Decay of the considered radioactive samples.

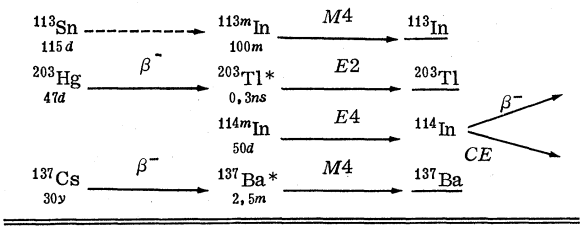

TABLE II. Measured energy of the observed hypersatellite lines. SSD: Solid-state detector.

Element	Energy (keV)	Method
InK_α^h	24.79	SSD
BaK_α^h	32.95	SSD
$TlK_{\alpha_1}^h$	74.12	SSD
$K_{\alpha_2}^h$	74.035	SSD

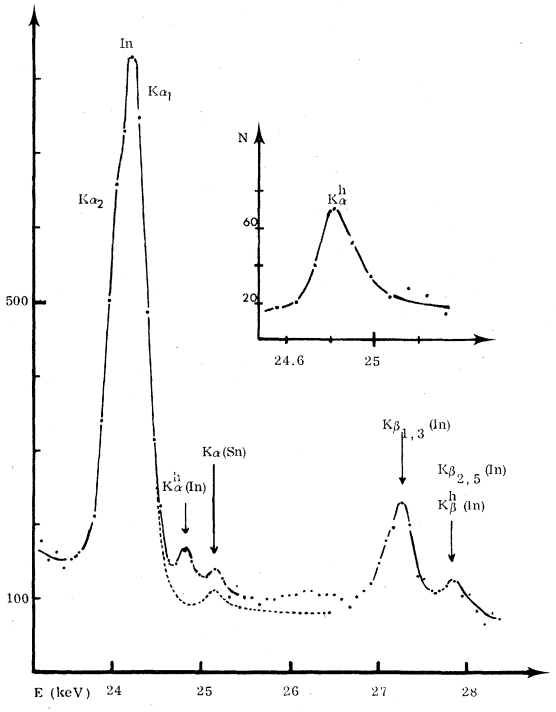

FIG. 1. K-hypersatellite spectrum of ^{113}In (Z=49).

TABLE III. Experimental values.

Nuclide	Our results $P_{KK}/P_K \times 10^4$	Other authors $P_{KK}/P_K \times 10^4$	Method	Ref.
^{113m}In	1.0 ±0.3	<0.2	e^-, e^- coincidence	18
^{114m}In	1.1 ±0.3	<0.17±0.03	e^-, e^- coincidence	19
^{137}Ba	0.7 ±0.3	1.8 ±0.5	e^-, e^- coincidence	20
^{203}Tl	0.14±0.3	0.4 ±0.15	$X_K - X_K$ coincidence	21

a very high-resolution detector both $K^h_{\alpha_1}$ and $K^h_{\alpha_2}$ can be observed and their intensity can be estimated with good confidence because of the relatively low background.

The results of Table III suggest two other remarks:

(i) All experiments previously reported for In and Ba were performed using e^-e^- coincidence devices. Furthermore the aim of those experiments was the observation of a second-order nuclear de-excitation process called "double internal conversion" (DIC). Following this phenomenon, the de-excitation of a nuclear state is thought to be able to take place through emission of two quanta which share the available energy, each of which can be converted. This electron spectrum is thus continuous in energy and of very weak intensity. For this reason most authors could only fix an upper limit of the phenomenon probability.

(ii) A drawback of the observation of the hypersatellite is that any process leading to double ionization will be indistinguishable. Thus, DIC., if observable, will also contribute to the intensity of the hypersatellites. In fact the most reliable experiment concerning DIC is that of Vukanovic *et al.*[19] in ^{114}In. Their result, 1.7×10^{-5}, is about one order of magnitude less than what we found for the total intensity of double-K ionization. It seems thus reasonable to neglect this phenomenon.

IV. COMPARISON WITH THEORY

A. Influence of the energy, nature and multipolarity on the double ionization probability during internal conversion

(i) The first point to be discussed is the influence of the energy of the ejected electrons, on the probability of double-K-vacancy production. This can be done in comparing the relative probability P_{KK}/P_K for the two different isotopes of Indium: ^{113m}In and ^{114m}In. As pointed out in Sec. I the double-K-vacancy production, in many electron atoms, is mainly due to shake-off processes (both electrons are ejected into the continuum) and one must take into account the energy of these ejected electrons when using the shake model, the sudden approximation not being used unless for very large velocities. It has been experimentally proved[24], that due to the decrease, at low velocities, of the density of available final states, the shake-off probability is substantially reduced when the energy of the faster ejected electron is significantly less than of the binding energy. The total P_{KK}/P_K probability summed over the whole energy spectrum will then be reduced, when the total available energy of the transition E_0 is not much larger than the threshold energy, the contribution of the low-energy part of the spectrum being relatively more important. This point has recently been discussed in detail by Mukoyama and Shimizu[25] who calculated the shake-off probability in the most direct way in the case of internal conversion. The relative probability of double-K-vacancy production leading to the emission of one electron with an energy E, in a dE interval, is equal to

$$P_{KK}/P_K\,(E)\,dE = |\langle \Psi^f_\epsilon \;|\Psi^i_K\rangle|^2\, S(E)\,dE,$$

where Ψ^i_K corresponds to the initial state (one bound electron in the K shell) and Ψ^f_ϵ to the final state (one electron in the continuum). $S(E)$ reflects the density-of-final states when taking account of the energy dependence of the differential internal-conversion coefficient $[\alpha = \alpha(E)]$ for the given γ transition (effect of the nature and multipolarity of the transition). P_{KK}/P_K obtained by summing this differential relation over the energy range, is then simply the product of the asymptotic value (sudden approximation) and of a given coefficient R that depends only on the energy, the nature and multipolarity of the transition

$$P_{KK}/P_K = |\langle \Psi^f_\epsilon \;|\Psi^i_K\rangle|^2\, R(E_0, n, \pi).$$

This $R(E_0, n, \pi)$ coefficient is then very close to one for large energy γ-ray transition.

Since the γ-ray transitions for the two-indium isotopes are different both in their energies and multipolarities, one might expect to observe different relative probabilities for producing double-K vacancies. Mukoyama and Shimizu calculated this R factor for ^{113}In and ^{114}In for which they found, respectively, 0.55 and 0.29. Not considering the absolute values of the probabilities

which will be discussed later, one can expect that the double-K-vacancy production should be roughly twice as large for ^{113}In as for ^{114}In, in contradiction with our experimental results, that lead to an equal probability for these two isotopes.

In fact one must also consider the effect of the direct Coulomb interaction (collision of the ejected electron with the atomic cloud) that has not been taken into consideration in these calculations. This effect is difficult to estimate and plays an important role at low energy (i.e., when the energy of the considered electron is close to that of the binding energy). Feinberg, in the case of β decay,[2] estimated that the probability of this effect relative to that of the shake process is of the order of the ratio of the K-binding energy over the maximum energy of the β particle. This process which increases the P_{KK} probability at the lowest energy must then increase the R factors and may explain at least partly, the observed discrepancy (see Tables III and IV).

B. Z dependence of the double-K ionization during internal conversion

We shall now compare the absolute values of the probabilities we have measured with various calculations first to emphasize the role of Coulomb correlation in the double-K-ionization processes.

(i) First of all we can compare our results with extrapolated values of Carlson's calculation for shake-off probabilities in rare gases after photoionization[27]. It appears (see Table V) that calculated values are systematically lower (about a factor of 7) than our experimental results.

This discrepancy is not surprising because the shake model in the single-particle approximation does not take into account the correlation effects which are very important when considering electrons in the same shell. This was first pointed out by Carlson[3] himself who found that the double $2p$-ionization in neon is seven times more probable than predicted by the shake model in the Hartree-Fock approximation. What we now find is that the correlation effects seem to be of the same order of magnitude in both cases.

(ii) Among the various possible methods taking, at least partly, into account the correlation effects one can make use of the generalized shake model of Åberg. In this method briefly described in Sec. II, overlap matrix element is calculated by using parametrized wave functions of the Hylleras-type instead of Hartree-Fock wave functions. In such a case the correlation effects between the two K electrons are taken into account but the two ejected electrons are considered as completely independent (the correlation effects are not taken into account in the final state). Then when one calculates explicitly the probability that single ionization occurs, $|\langle\Psi_K^f|\Psi_K^i\rangle|^2$, it is necessary to calculate also explicitly the shake-up contributions that have to be substracted. Such calculations have recently been make by Åberg and Peltonen[10] and are presented in Table V. It is then now possible to make two remarks. The first remark is that there is now a reasonable agreement between Åberg's calculations and our experimental data. The second is that there is a constant factor, over a large range of Z values between Carlson and Åberg's calculations which means again that the correlation effects play a similar role for all the elements. This is in fact not very surprising because in double-K-ionization processes one electron is "pushing the other" and the relative correlation effect is probably the same for any element (Z being a scaling factor.) The correlation effects, which rapidly decrease as a function of Z when calculating energies, are then in our case constant over Z when studying the relative movement of both electrons.

(iii) In Åberg's calculation no attempt has been made to include relativistic effects which likely affect the wave-function overlap. These relativistic corrections have been recently studied by Mukoyama and Shimizu.[23] These authors have made a comparison between nonrelativistic Hartree-Fock wave functions and relativistic hydrogenic wave function with some appropriate screening factors. They found that relativistic corrections strongly increase the double-K-ionization probability and in such a manner that their predictions are also now in good agreement with our experimental values (see Table V). Surprisingly the ratio of their relativistic and nonrelativistic calculations seems to be roughly constant over Z for elements between iron and thallium so that these relativistic corrections in the overlapping of the wave functions play a similar role to that of correlation effects in Åberg's calculation. In fact, one should make use, in any case, of both types of correction. Nevertheless it seems to be possible to compare some of our results with these various calculations namely for the elements of Z numbers close to 50. As previously quoted

TABLE IV. Decay characteristics of indium isotopes.

	Nature and multipolarity	Energy (keV)	B_K (keV)	P_{KK} Mukoyama calculation 25
^{113}In	$M4$	393	27.9	3.93×10^{-5}
^{114}In	$E4$	192		2.06×10^{-5}

TABLE V. Comparison of our experimental results with various theoretical predictions. OSM: One-step model of Mukoyama, i.e., shake-off corrected by the energy factor. Åberg: 204 parameter Hylleraas-type wave function of K. Aashamar.

	$P_{KK}(10^{-4})$				
	Our experimental values	Carlson (5) (26) corrected	Åberg (10)	Mukoyama (23)	Mukoyama (23) OSM
$^{113m\text{-}114}$In ($Z=49$)	1 ±0.3	0.1	0.37	0.707	0.393 and 0.206
^{137}Ba ($Z=56$)	0.7 ±0.3	0.09	0.28	0.603	0.376
^{203}Tl ($Z=81$)	0.14±0.3	0.055	0.14	0.458	0.363

it seems that Coulomb correlation effects play a constant role over Z and that Åberg's calculations have to be increased if both corrections are additive (which is not obvious); Since Åberg's values are smaller than our experimental ones by a factor of 2, it seems that the necessary relativistic corrections may lead to a good agreement with the experiment.

(iv) The above considerations cannot apply in the case of very heavy atoms like Tl ($Z=81$) where these simple relativistic corrections are not sufficient to take into account the whole relativistic effects. For these very heavy atoms in which the distance between the two K electrons is very small the magnetic interaction between both magnetic moments can no longer be neglected in comparison of the electrostatic repulsion energy that only varies as Z. The Coulombic correlation effects between the electrons that appear at the shortest distances are then sensitively affected in a very complicated manner due to the change of the sign of the interaction energy as a function of instantaneous relative orientation of the spins. If such an interaction at the shortest value of approach of the two electrons in an antiparallel arrangement should lead to a negative (attractive) magnetic energy, this should then decrease the effect of the Coulombic repulsive force and strongly change (decrease) the P_{KK} probability value. In any case it does not seem to be possible at the present state of the theory, which cannot take into account these spin-spin correlation effects, to get a precise estimate of the double-K-vacancy production for heavy elements, comparable to experimental values. In the case of very heavy or super heavy elements like those studied in heavy-ion collisions, in which the spin-spin energy can be equal to that of the electrostatic repulsive energy, these effects should be very important and should play a crucial role in the quasimolecule behavior.

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