Electron spectra of europium vapor

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The spectra of electrons scattered at 90° by europium atoms were investigated, and the energy dependence of the elastic differential cross section has been determined. The cross section exhibits resonance features associated with short-lived states of negative europium ions. The electron spectra of autoionizing states were found to contain 90 lines due to multichannel decay of atomic and ionic states.

INTRODUCTION

Published data on the excited states of europium atoms were obtained mainly by optical methods. Both emission and absorption spectra were used to analyze the structure of energy levels. It will be useful at this point to note some of the results published in recent years.

Photoabsorption spectra were investigated by Smith and Tomkins[1,2] with high resolution in the wavelength range 7200–2100 Å. More than 350 lines were observed, and most of them were identified. This and previous work served as a basis for the tabulations of the energy levels of europium atoms and ions that are given in Ref. 3 and contain data on more than 500 energy levels of the atom. Whereas the identification of levels lying below the ionization limit can be said to be sufficiently reliable, the examination and identification of the autoionizing states (AIS) is found to encounter considerable difficulties.

The photoionization spectra of europium vapor were analyzed by Parr.[4] Although the spectra were recorded in the range 2189–1350 Å, a small number of discrete lines was observed in the narrow spectral range 2189–1850 Å, and the strongest of these lay between 2189 and 2100 Å, i.e., in the immediate neighborhood of the continuum limit.

The largest number of discrete lines above the continuum limit was observed by Kozlov *et al.*[5] in the photoabsorption spectra. The maximum separation of the lines from the ionization limit ($E_i = 5.67$ eV) is 3.9 eV. However, most of the lines cannot be identified because, as noted in Ref. 5, the "intensity of the absorption lines and their profiles are such that it is impossible to isolate some group of lines or series." All that can be said is that they are due either to two-electron excitation in the $6s^2$ shell or the excitation of inner f electrons.

The formation of AIS associated with the excitation of the deeper $5p^6$ subshell is possible in addition to the processes mentioned above. Such states were seen by Tracy,[6] who used an absorption setup in which a 0.5-GeV synchrotron was used as the source of incident radiation. A large number of discrete absorption lines was recorded in the range ~20.3–31 eV. This energy range is characterized (as for other rare-earth elements) by the presence of a broad and strong "giant" resonance lying at about 27.5 eV. However, in contrast to other elements, the europium resonance has a flatter top, and the lines lying above it are practically unresolved. The spectral lines were not identified for the same reason as in the case of the low-lying AIS. It is considered that the europium spectra take the form of a superposition of many series that converge to a large number of closely spaced limits, and it is this that is responsible for the rather broad profile of the "giant" resonance and for the fact that lines lying above it have not been resolved. Moreover, we note that Tracy[6] does not report accurate values for the line energies, and approximate data on these energies can be obtained only by examining the scale reproduced under the spectrum.

The application of electron beams to the study of the excited states of europium atoms and ions began in our country. Thus, Shimon *et al.*[7] measured the excitation functions for the 22 strongest optical transitions excited by electrons with energies ranging from threshold to 300 eV. Absolute cross sections and their energy dependence were established.

Electron spectroscopy was used to investigate the decay of autoionizing states in the sole paper by Alekhsakin *et al.*[8] For electron-beam energies in the range 60–500 eV, a total of 12 broadened lines due to the multichannel decay of states in the $5p^6$ subshells, and of ionic states, was detected. The line energies lie in the range 7–17 eV.

Despite definite advances in the study of the level structure of europium, and of electron-atom interaction processes, there are many unanswered questions. In particular, the spectra of electrons scattered by atoms have not been investigated, the energy dependence of the elastic cross section has not been measured, the electron spectra of autoionizing states have not been adequately studied, and there are no data on the optically forbidden transitions in the atom and the excitation energies of high-lying ionic states. These questions are examined in the present paper.

EXPERIMENTAL METHOD

The electron spectrometer, incorporating the 127-degree electrostatic energy analyzer, was described earlier in Ref. 9. As before, the collisions were investigated in a vapor-filled cell, using differential pumping of the electron-optical system consisting of the gun and the energy analyzer. The scattered and emitted electrons were observed at 90° to the incident beam, the analyzer resolution was about 0.05 eV, and the energy spread in the electron beam was about 0.3–0.5 eV. A typical beam current at 50 eV was 100 μA. The temperature of the reservoir containing metallic europium

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during the experiment was about 500–520°C, and the temperature of the cell and energy analyzer was 550°C or more. Under these conditions, the temperature of the electron detector (channel electron multiplier) did not exceed 200°C.

A set of electrostatic lenses mounted at the exit from the energy analyzer was used to reduce the background signal due to secondary emission of electrons from the surfaces of the spectrometer electrodes, to produce greater contrast in the discrete component of the spectra, and to increase the energy resolution in the spectra.

The electron spectra were recorded at constant energy resolution, i.e., for a fixed potential difference between the cylindrical electrodes of the spectrometer (0.5–1.5 V). They were scanned by applying a linear voltage ramp to the exit slit of the analyzer.

SPECTRA OF SCATTERED ELECTRONS

As noted above, a large number of closely spaced levels appears below the ionization limit of the europium atom, so that it may be expected that the spectra of scattered electrons would not be well-defined. However, this was not found to be the case. The recorded spectra (see Figs. 1 and 2) contain a small number of discrete lines and present a clear picture of not only the level structure, but even the relative probability of their electronic excitation. The observed states were identified on the basis of the results reported in the papers enumerated above. Table I lists the experimental level excitation energies E_a, together with the state symbols and the corresponding excitation energies taken from published tabulations.[3] The line energies were determined to within about 0.05 eV. To distinguish lines in the spectra of scattered electrons from those produced as a result of AIS decays, the latter are indicated by primes in Fig. 2. The scale along the ordinate axis is different for different spectra.

The undoubted advantage of this spectrometer is that it can be used to observe spectra from virtually the threshold energy, so that one can follow the evolution of the lines and measure their intensity as a function of energy.

The lowest-lying lines 1 and 2 are the first to appear as the energy E of exciting electrons is increased. The total excitation cross sections were measured in Ref. 7 for the

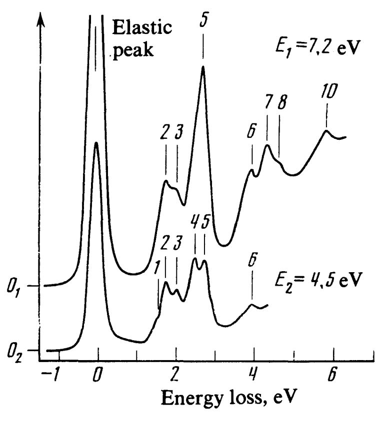

FIG. 1. Spectra of electrons scattered by europium atoms for beam energies of 7.2 and 4.5 eV. $\theta = 90°$.

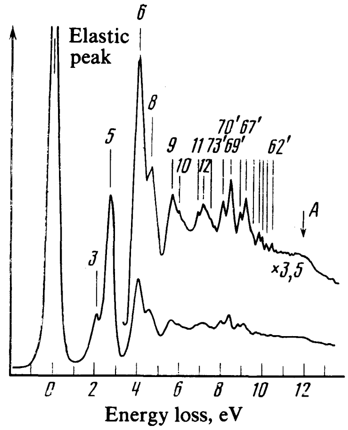

FIG. 2. Same as Fig. 1 for beam energy of 22 eV.

$4f^7 6_s 6_{pz}\, ^{10}P_{7/2,\,9/2}$ levels. These cross sections reach a maximum at $E = 4.4$ eV, and fall rapidly thereafter. We use this to explain the fact that line 2 in our spectrum appears only for energies $E < 10$–15 eV (see Figs. 1 and 2). When $E > 10$ eV, this region is dominated by line 3, and line 2 becomes practically unresolved. The intensity of line 2 increases similarly, so that, even at very low energies, line 1 rapidly becomes unresolved. The cross sections for transitions from the $4f^7 6_s 6_{pz}\, ^8P_{5/2-9/2}$ levels measured in Ref. 7 reach their maximum values ($Q_{max} = 20\times10^{-19}$–$40\times10^{-19}$ cm^2) for $E = 6$–11 eV, and thereafter fall slowly with increasing energy.

Line 5 is the strongest line in the spectrum. At the same time, the cross sections for transitions from the $4f^7 6_s 6_{py}\, ^8P_{5/2-9/2}$ levels are the largest among all the values ($Q_{max} = 120\times10^{-19}$–$560\times10^{-19}$ cm^2) for beam energies of 15–20 eV. The correlation with the data reported in Ref. 7 is thus complete.

Line 4 is observed only at low energies and competes in intensity with line 5. As the energy increases, it cannot be resolved from the stronger line 5, but, when the energy reaches 16 eV, line 4 can again be resolved from the comparable (in intensity) line 5. It vanishes again as the beam energy is increased further. All this indicates that the excitation cross sections for the $4f^7 5d\, 6_s b\, ^8D$ levels have a complex energy dependence.

Line 6 is really a whole group of lines (see Table I). It has a low intensity for $E \leqslant 10$ eV (see Fig. 1), but it becomes stronger for $E > 10$–20 eV. At the latter energies, the intensity of line 6 is inferior only to line 5 (see Fig. 2).

Line 7 has the dominant intensity among lines 6–8 for $E < 10$ eV, but becomes indistinguishable from the stronger lines 6 and 8 at higher energies (Fig. 2).

Line 9 lies in the immediate neighborhood of the ionization limit, and is due to the presence in the atom of a large number of closely spaced $4f^7 6snp$ levels.[3] Line 10 appears before line 9, but its intensity subsequently becomes much lower than that of the latter line (see Figs. 1 and 2). It is possible that this behavior of the intensity of line 10 can be explained in terms of the presence of optically forbidden states in this region.

TABLE I.

Line number	E_a, eV	State	E_a, eV [3]
1	1.60	$4f^75d6sa^{10}D_{5/2-9/2}$	1.60–1.64
2	1.74	$4f^76s6pz^{10}P_{7/2-9/2}$	1.74–1.80
3	2.01	$4f^76s6pz^8P_{5/2-9/2}$	1.97–2.06
4	2.46	$4f^75d6sb^8D$	2.41–2.46
5	2.70	$4f^76s6py^8P_{5/2-9/2}$	2.66–2.70
6	4.02	$4f^75d6py^{10}P_{7/2-11/2}$	4.02–4.08
		$4f^75d6pz^{10}D_{7/2-13/2}$	3.86–3.98
		$4f^75d6pz^8F_{1/2-13/2}$	3.93–4.06
7	4.35	$4f^75d^{2\,8}D_J$, ^8P_J	4.33–4.40
8	4.63	$4f^65d6s^2$ (132–146)	4.59–4.72
9	5.58	$4f^76snp$ (n=12–42)	5.46–5.66
10	5.88	$4f^75d7p^8P$	5.72–5.86
		$4f^76snp$ (n=44–67)	5.87
11	6.77	?	6.70
12	7.11	?	–

Line 11 can be compared with an unidentified state with excitation energy[3] $E_a = 6.70$ eV. Line 12 has a high intensity (see Fig. 2). The nearest (in energy) broad line in the photoabsorption spectra[5] has an excitation energy of 7.33 eV. It is possible that, here again, we are dealing with the excitation of optically forbidden transitions, especially since the intensity of line 12 falls slightly for $E > 22$ eV.

Thus, most of the lines in the spectrum of scattered electrons are due to the excitation of a single external s electron to different final states. An analogous situation was observed in the case of the optical spectra of europium excited by electron impact.[7] The presence of strong lines lying beyond the single-ionization limit, and effectively excited by electrons with energy close to the threshold, is an argument in favor of the presence of low-lying optically forbidden ionization states in europium.

ELASTIC SCATTERING

Since the lines in the electron energy-loss spectrum of europium usually have a complex structure due to the simultaneous excitation of several levels in one or even several configurations, we confined our attention to a qualitative examination of the spectrum, and did not measure the line intensity as a function of energy. On the other hand, the spectral line corresponding to elastic scattering of electrons is free from overlap, and its intensity can readily be measured as a function of energy. Figure 3 shows the measured dependence for energies in the range 1–10 eV. The energy scale under the curve was calibrated to better than 0.1 eV

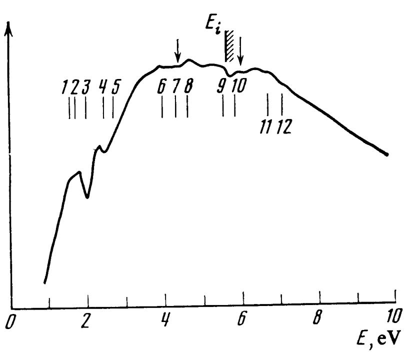

FIG. 3. Elastic differential cross section for electrons as a function of energy.

against the threshold for the appearance of a current in the collision region, using the halfwidth at full height of the instrumental function. However, we cannot guarantee absolutely the observed shape of the curve in a broad energy range because the variation in the transmission of the spectrometer with energy was not taken into account. On the other hand, we were interested only in the fine structure within narrow energy intervals, comparable with the width of the electron energy distribution function.

It is clear from Fig. 3 that the energy distribution of the elastic differential cross section of europium atoms exhibits a series of narrow features—resonances—due to the formation and decay in the course of collisions of short-lived states of negative europium ions Eu^-. The first indication of the existence of these resonance states in europium were reported by the authors of Ref. 7, who observed a fine structure on some line excitation functions. For example, the excitation cross sections obtained for four different lines were found to reach a maximum at the same energy $E = 4.4$ eV, which suggests that the ion Eu^- has an energy level at this value. A feature near this energy can also be seen in the differential cross section (see Fig. 3). Another feature in the line excitation cross sections occurs near 6 eV and it, too, can be compared with a feature on the elastic cross section curve. The positions of the peaks on the optical excitation functions[7] are indicated by the arrows in Fig. 3.

Since the atom has a large number of energy states, it is difficult to identify the initial states for these resonances. However, we assume that the strongest resonances in the cross sections occur near effectively excited atomic levels, and use vertical bars in Fig. 3 (cf. Table I) to indicate the measured energy loss. As can be seen, the cross sections exhibit rapid changes near practically all these levels. The strongest resonance in the elastic cross section is observed at $E = 2.1$ eV. It lies in the immediate neighborhood of the excitation thresholds for the $4f^76s6pz^8P_{5/2-9/2}$ levels ($E_a = 1.97$–2.06 eV). The total excitation cross sections for these levels reach their maximum at energies of 6–11 eV, but it is the excitation thresholds for these levels that have a stronger effect on the elastic cross section than the maxima on the excitation cross sections. Departures from monotonic variation of the cross section are also noticeable near the lower-lying levels 1 and 2. The energy of line 4 occurs at a minimum of the differential cross section. On the other

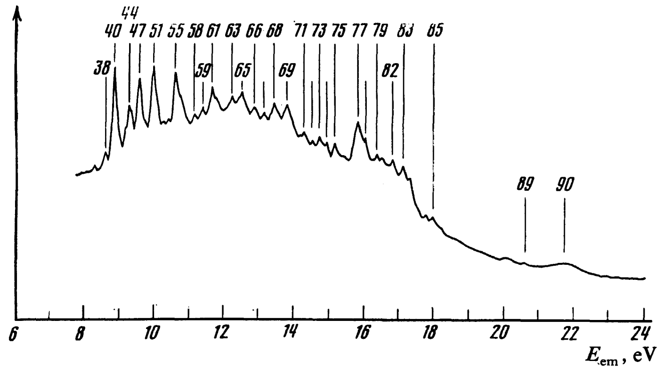

FIG. 4. Spectrum of emitted electrons for electron beam energy of 120 eV.

hand, a minimum of the elastic cross-section curve may be looked upon not as a new resonance, but as a manifestation of a convolution of the potential part of the cross section and a resonance in the form of a combination of a minimum and a maximum. It is interesting that the elastic cross section does not exhibit any noticeable changes near the $4f^76s6py^8 P_{5/2-9/2}$ levels that have the highest excitation probability under electron impact. Resonance features of the excitation functions for these levels were not seen in Ref. 7 either. We note that the shape of the energy dependence of the elastic differential cross section is similar to the analogous result for ytterbium atoms.

We may thus conclude that the formation and decay of short-lived states of the negative ions Eu^- play a definite role in the population of atomic levels, and influence the energy dependence of the elastic scattering cross section.

SPECTRA OF AUTOIONIZING STATES

Figures 4 and 5 show portions of the electron spectra emitted by europium atoms and ions during the decay of autoionizing states. The primary beam energy was in the range 15–500 eV, and the energies of the emitted electrons were in the range 0–24 eV. No discrete lines were seen above 24 eV.

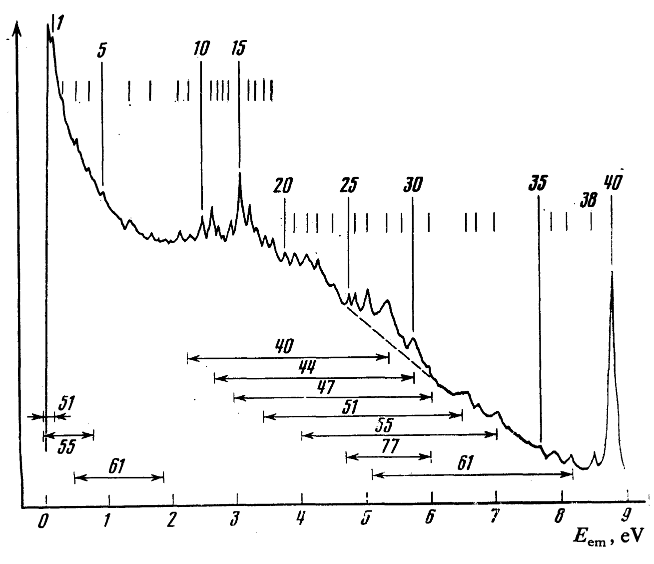

FIG. 5. Low-energy portion of the spectrum of emitted electrons for electron-beam energy of 200 eV.

Since in the analogous paper[8] the absolute energy scale was determined only approximately, and there is no information on the Auger transition energies, and since contact potentials in the spectrometer complicate the direct determination of line energies, we had to face the serious problem of energy calibration. Accurate line energies are essential for subsequent interpretation. This problem was solved by simultaneously recording the spectra of two elements with similar vapor pressures. The spectrometer cell was supplied by two reservoirs, one containing europium vapor and the other the comparison element (ytterbium). A set of electrical heaters and thermal shields enabled us to maintain the necessary temperature state for long period of time. The electron spectra of ytterbium (see, for example, Ref. 10) are characterized by the presence of two strong lines at 12.91 and 8.57 eV, respectively. They correspond to the Auger decay of the $[5p^54f^{14}6s^2\ ^2P_{3/2}]$ state of YbII to the ground $5p^64f^{14}\ ^1S_0$ and excited $[5p^64f^{13}(^2F_{7/2})5d_{3/2}]_{J=3}$ states of YbIII. A few lines of very low intensity lie between these two lines. The spectrum recorded for the yttrium/ytterbium mixture shows that the strong europium lines (lines 40–61) appear exactly in this interval. We determined the energy of the strongest line 40 as being 8.82 ± 0.01 eV. The previous estimate of this energy[8] was about 7.5 eV. Table II lists the energies of 90 most reproducible europium lines. The energy values indicated in the table are averages over a large number of spectra.

DECAY OF ATOMIC STATES

We shall now consider the decay of autoionizing states in the $5p^6$ subshell. Transitions from it to the ground state of the singly-charged EuII ion should be accompanied [6] by the emission of electrons with energies of 14.6–25 eV. Such lines were, in fact, present in our spectrum (see Table II). Two resonance windows were noted in the photoabsorption spectra [6] at energies of 17.6 and 19.4 eV, measured from the ionization limit. It is interesting to note that the spectra of emitted electrons contain well-defined lines only below the first resonance window. The intensities of the lines and of the background are found to fall in the region of this window (see Fig. 4). Several low-intensity lines can be seen between 17.6 and 19.4 eV. The strongest narrow lines of the photoabsorption spectrum are represented in the electron spectrum by lines 83 and 84. Table II shows agreement between the energies of lines in our spectrum and in the spectra reported in Ref. 6.

Another interesting feature of the electron spectra of europium is that they contain the well-reproducible broad line 90, which corresponds to the decay of the "giant" resonance in the photoabsorption spectrum, to the ground state of EuII. Our value for the excitation energy of this resonance state is 27.47 ± 0.05 eV, which is in good agreement with Ref. 6. The line is most efficiently excited at high beam energies but, even then, it has lower intensity than the other lines in the spectrum. We note that an analogous transition is not observed in ytterbium spectra.[10]

The strongest line in this energy range is line 77. Because of its anomalously high intensity, we ascribe it to the

TABLE II.

Line	E_{em}, eV	Line no.	E_{em} eV	E_a, eV	Line no.	E_{em}, eV	E_a, eV	[6]
1	0,24	31	5.97		61	11,65	28,56	–
2	0,33	32	6.58		62	11,82	18,79	–
3	0,53	33	6.72		63	12,10	19,11	–
4	0.73	34	7,01		64	12,32	20,00	–
5	0,93	35	7.66		65	12,50	19.49	–
6	1.35	36	7.90		66	12,88	19,91	–
7	1.68	37	8,15		67	13,12	18,79	–
8	2,12	38	8.52		68	13.44	19,11	–
9	2,29	39	8.73		69	13.82	19,49	–
10	2.46	40	8.82	25,73	70	14,24	19.91	–
11	2.63	41	8,93		71	14,33	20,00	–
12	2.75	42	9,09		72	14,48		–
13	2,82	43	9,15		73	14,67	20,34	?
14	2,92	44	9.23	26,14	74	15,02	20,69	?
15	3.06	45	9,32		75	15.20	32,11	–
16	3.22	46	9,47		76	15,38	32,29	–
17	3.33	47	9.52	26,43	77	15,86	32,77	+
18	3,47	48	9.63		78	16,05	21,72	+
19	3.59	49	9.73		79	16,30	21,97	+
20	3.76	50	9.88		80	16,57		–
21	3,92	51	9.96	26,87	81	16,78		–
22	4.11	52	10.10		82	16,85	22.52	+
23	4.27	53	10.35		83	17,14	22,81	+
24	4.51	54	10,51		84	17.33	23.00	+
25	4.75	55	10.57	27.48	85	18,00	23,67	+
26	4.84	56	10.66		86	18.66	24,33	+
27	5.03	57	10,81		87	18.95	24,62	+
28	5.34	58	11,13		88	20,17	25.84	+
29	5.56	59	11.33		89	20,66	26.33	+
30	5.73	60	11.52		90	21,80	27.47	+

Auger decay of an ion state (see below). The multichannel decay of states in the $5p^6$ subshell to excited $4f^6 5dnl$ states of Eu II should produce whole groups of lines with a minimum energy of about 6 eV. It is possible that the series of low-intensity lines for $E_{em} > 6$ eV is, in fact, due to this process. However, because of the absence of reliable information on the excitation energies of states in the $5p^6$ subshell and their classification, we shall not be able to analyze these transitions.

The third feature of the electronic spectra of the $5p^6$ subshell is the presence of lines that cannot be explained in terms of the decay of states known from photoabsorption spectra.[6] These are lines 62–76. Only two of them, namely, 73 and 74, can be compared with lines in the optical spectra whose energies are about 20.3 eV (weak) and 20.7 eV (strong). The energies of lines 75 and 76 correspond to the segment of the photoabsorption spectrum that contains no lines. Line 72 was seen by us only at high beam energies.

To explain the origin of these lines, we investigated the behavior of their intensity in a broad energy range. We found that the intensity rose rapidly as we approached the threshold of about 19–20 eV for these lines. Such threshold energies indicate that we have been dealing with an atomic decaying state. The energy dependence of some of these lines is shown in Fig. 6. It is clear from this figure that some of the line intensities increase by a factor of 10–100 near the threshold. This is characteristic for lines produced as a result of the decay of optically forbidden autoionizing states.

It would appear that, by adding the ionization energy of the atom to the line energy, it should be possible to determine the excitation energy for the states found above. However, this was not the case at all. We noted that there were two groups of lines of different intensity: lines 67–70 and 62–65 or 66, the energies of which differ from one another by roughly the same amount, namely, about 1.3 eV. This suggested to us that we were dealing with, at least, the two-channel decay of an autoionizing state to the ground $4f^7 6sa^9S_4$ and excited $4f^7 5da^9D_{4-6}$ states of Eu II, lying at 1.28–1.38 eV above the ground state of Eu II.

However, the line energies are not sufficient to enable us to confirm the possibility of multichannel AIS decay: we also need the thresholds for the appearance of these lines in the spectra. We have therefore carried out a series of experiments in which we made a detailed examination of the threshold behavior of the line intensities. The result of one such experiment is given in Fig. 7, which clearly demonstrates the existence of the same threshold for several lines. For comparison, Fig. 7 also shows the proposed appearance thresholds for all the lines. These are defined as $E_{ap} = E_{em} + E_i$. The intensities of all the lines reach their maxima for

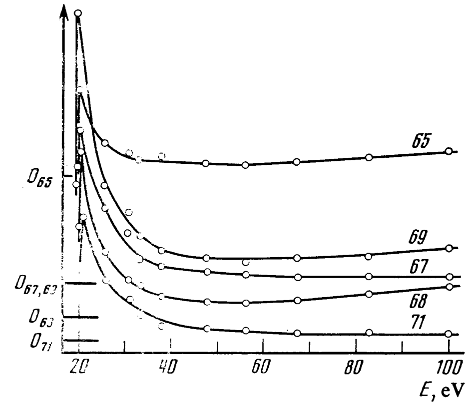

FIG. 6. Energy dependence of the intensity of a number of lines in the spectrum of emitted electrons (number shown against each curve is the corresponding line number in Table II).

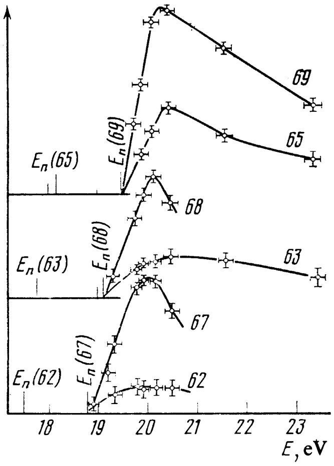

FIG. 7. Energy dependence of the intensity of six lines near the threshold.

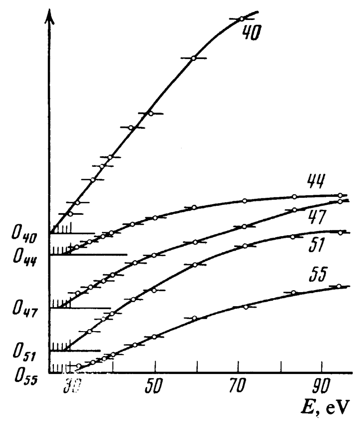

FIG. 8. Energy dependence of the intensity of ionic lines.

beam energies of about 20–20.5 eV, which may well be related to the presence of a state of the negative ion Eu^- near these energies. The decay of this state may additionally populate the autoionizing levels. Lines 71 and 64 may be treated as due to the decay of an optically forbidden autoionization state with excitation energy $E_a = 20.00$ eV to the ground and the lowest-lying excited $4f^7 6sa\,^7S_3$ state of the Eu II ion for which $E_a - E_i = 0.21$ eV.

The above experimental factors enable us to conclude that the europium atom has optically forbidden states in the $5p^6$ subshell that are effectively excited by electron impact. Their excitation energies have been determined and the decay channels suggested. It would appear that this is the first clear demonstration of the possibility of effective multichannel decay of an autoionizing state.

As for the low-lying atomic autoionizing states that occur during the excitation of f and s^2 electrons, their existence would explain the origin of only the first few lines in the spectrum (see Fig. 5 and Table II).

AUGER DECAY OF IONIC STATES

The strong spectral lines recorded for beam energies in excess of 40–50 eV were due to Auger decays of ionic states. As noted in Ref. 8, states belonging to the $5p^5 4f^7 5d\,(^3P)6s$ and $5p^5 4f^7 5d\,(^1P)6s$ configurations, and the $5p^5 4f^7 6s^2\,^2P_{3/2,\,1/2}$ levels, lie above the double-ionization limit of the atom, and decay effectively with the formation of an electron and the doubly charged ion Eu III. The lowest-lying levels among those belonging to the $5p^5 4f^7 5d\cdot(^3P)6s$ configuration occur at about 24 eV.[8] Accurate measurements of line energies corresponding to the decay of such states (lines 40, 45, and 50) enabled us to determine their excitation energies. These results were obtained on the assumption that the AIS decay occurred to the ground $5p^6 4f^7\,^8S_{7/2}$ state of Eu III. They are listed in Table II. Their intensities were then measured as functions of energy (see Fig. 8) in order finally to settle the nature of these lines. The resulting curves are monotonic and reach a broad maximum at 100–150 eV. This behavior is characteristic for Auger transitions in other elements.[10] The observed line appearance thresholds are in reasonable agreement with values calculated from $E_{ap} = E_{2i} + E_{em}$, where E_{2i} is the double ionization energy of the atom (16.91 eV). This confirms the assumed AIS decay to the ground state of Eu III.

Detailed examination of the interval containing lines 38-56 revealed a further series of closely spaced lines that are probably due to the decay of both ionic $5d\,(^3p)6s$ states and atomic states in the $5p^6$ subshell. The increase in the intensity of atomic lines at energies below 30 to 35 eV impedes the precise determination of the appearance thresholds the ionic lines.

The $5p^6 4f^7 6s^2\,^2P_{3/2}$ ionic state lies close to the "giant" resonance.[8] If we add the double ionization energy to the energy of line 55, we obtain 27.48 eV as the excitation energy, which agrees to within 2.5 eV with the measured value (Fig. 8). The precision of the measured line-appearance threshold cannot be improved because of the low line intensity near the threshold, and the superposition of atomic lines.

The $5p^5 4f^7 5d\,(^1P)6s$ levels lie above the $5p^6 4f^7 6s^2\,^2P_{3/2}$ state at energies of 29–31 eV,[8] and are adjacent to the $5p^6 4f^7 6s^2\,^2P_{1/2}$ state of the Eu II ion. The decay of these states should be accompanied by the emission of electrons with energies in the range 12–14 eV. Lines 61 and 68 dominate the adjacent interval of emitted-electron energies for beam energies in the range 50–100 eV. One can be fairly confident that line 61 is due to decay from one of such states. On the other hand, lines appearing as a result of the decay of the lower-lying $5d\,(^1P)6s$ levels are found to superimpose on lines due to states in the $5p^6$ subshell of the atom. However, their presence in the spectrum can be demonstrated as follows. At energies above 40 eV, there is an increase in the intensity of some of the lines that result from the decay of optically forbidden states in the $5p^6$ subshell (Figs. 4 and 6), which we interpret as being due to the superposition upon them of Auger-decay lines. Moreover, lines 75 and 76, which do not fit into the level scheme of the $5p^6$ subshell,[6] can also be ascribed to ionic transitions.

Finally, we consider that line 77 is due to the decay of the $5p^6 4f^7 6s^2\,^2P_{1/2}$ state of Eu II. If this is so, the level excitation energy is 32.77 eV, and the spin-orbit splitting of the $^2P_{3/2}$ and $^2P_{1/2}$ levels is 5.29 eV. We have noted that the structure at $E_{em} = 16$ eV does not vanish for $E = 32.77$ eV, but this can be explained by the presence of lines due to the $5p^6$ subshell, with similar energies.[6]

Since ionic states in the $5p^5 4f^7 5d\,6s$ and $6s^2$ configurations have higher energies than most of the known[3] excited states of the doubly-charged europium ions, they can decay by the multichannel process, with electrons and excited doubly-charged ions as the byproducts. This process is currently regarded as an additional mechanism for producing doubly-charged ions in different quantum states. Comparison of the excitation energies of EuII states determined above with the data on the excitation energies of EuIII states[3] shows that this type of Auger decay should be accompanied by the emission of electrons with energies of 0–12 eV. Most of the lines we have recorded appear in this energy range.

The tables in Ref. 3 contain about 100 excited states of EuIII, so that the number of combinations between the upper and lower levels participating in the transitions is enormous. In the absence of the necessary theoretical calculations, we cannot even attempt a rigorous approach to the interpretation of the multichannel processes. We merely cite some of the features that we have noted.

It is interesting that the excited states of EuIII appear in two groups.[3] One of them occupies the interval 3.49–6.56 eV above the ground $^8S_{7/2}$ state, and the other lies in the range 9.79–11.18 eV. The multichannel decay of EuII states at 26.7 V above the ground state of EuI must therefore be accompanied by the emission of two groups of lines. Thus, the decay of the $^2p_{1/2}$ state leads to the appearance of lines with $E_{em} = 9.30$–12.37 eV and 4.68–6.07 eV. The EuII($^2P_{1/2}$)→EuIII($4f^6 5d\,^8H_J$) transitions can successfully explain the origin of lines 57–61. Moreover, the decay of the $5d\,(^1P)6s$ state contributes to the formation of line 61, and this is responsible for its high intensity. Transitions from the $^2P_{1/2}$ state to the lowest excited states of EuIII are difficult to observe because of the superposition of lines 53–65 upon them. The decay of the $^2P_{1/2}$ state to the high-lying group of EuIII states leads to the appearance of the well-defined group of lines 25–31 (see Fig. 5). Transitions from other levels superimpose on this group.

Examination of the region 0–8 eV shows that most of the lines in this region vanish from the spectrum when the primary beam energy is reduced to about 30 eV. They are most clearly defined at energies of 150–300 eV. They cannot therefore be a consequence of the decay of atomic states in the $4f^7$ and $6s^2$ subshells. Nor can they be a manifestation of the decay of states in the $5p^6$ subshell of the atom to the $4f^6 5dnl$ states of the singly-charged ion, since the latter have a low probability of decaying even to the ground state of EuII. The only reason for their appearance must be the multichannel Auger decay of ionic states to the states of Eu*III.

Figure 5 shows energy intervals for electrons emitted by EuII ions undergoing transitions to Eu*III states. The numbers identify the decaying ionic states (see Table II). The characteristic feature of the picture is that, for all the ionic states, there is a line due to a transition to the lowest-lying excited state of EuIII (see Fig. 5).

CONCLUSION

The experimental data that we have obtained clearly demonstrate the presence of multichannel processes in europium atoms and ions. Additionally, we note that, in contrast to YbII ions, the $^2P_{1/2}$ state of europium decays much more effectively to both the ground and the excited states of EuIII. It is possible that, in ytterbium, the radiative decay of the $^2P_{1/2}$ state predominates over autoionization decay.

Another distinguishing feature of europium spectra is the presence of the line corresponding to the autoionization decay of the "giant" resonance corresponding to the $5p^6$ subshell to the ground state of EuII, which is not seen in the ytterbium spectra.[10] One would therefore also expect to see the decay of this resonance to the excited $5d\,(^3P)6s$ states of EuII, which have lower energies. The expected transition energies are as follows: 0.63, 1.07, 1.36, and 1.77 eV. It is possible that lines 3–7 (see Table II) are, in fact, due to these processes. Line 6 has the closest energy value ($E_{em} = 1.35$ eV). It dominates the other lines by its intensity. We also note that the emitted-electron energy interval 0–2 eV occurs in the region of a considerable reduction in the transmission of the energy analyzer. This can be confirmed by inspection of Figs. 3 and 5. The true intensity of the lines examined above is therefore much higher. The energy defect of lines 3–7 can be explained by the complex structure of the "giant" resonance.

As in Ref. 10, we have measured the apparent ionization cross section of europium as a function of the primary-beam energy. The resulting curve demonstrates the presence of weak features near the ionization threshold and at about 20 eV. The former we associate with the autoionization of low-lying atomic states in the $4f^7$ and $6s^2$ subshells, and the latter with the decay of the optically forbidden states in the $5p^6$ subshell that were found above and are most readily excited by low-energy electrons.

Moreover, after the completion of the experimental part of this research, examination of a number of spectra recorded for beam energies of 20–30 eV revealed the presence of a number of lines with energies of 8–11 eV, which is either a consequence of the decay of the above forbidden AIS to highly-excited ionic states, or there are some unknown states of the atom with excitation energies of 14–17 eV.

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