amounts to (0.5 - 2) x 10^{-18} cm^2, which is much higher than the corresponding value for anthracene. According to a calculation of the levels of the pyrene molecule [2], two-photon transitions to the B_{1g} levels are allowed. The lifetimes at these levels are quite small compared with t_u. It follows also from the fluorescence spectra [5] and from the fluorescence decay time, that in the case of two-photon absorption excitations are accumulated at the lower singlet excited level of symmetry B_{3u}. Single-photon transitions from this level are allowed at the levels A_{1g} and B_{1g}. The energy of the ruby-laser quantum is close to the energy difference between B_{3u} and these levels. Consequently, the corresponding transitions are possible and have cross sections close to the resonance ones. Judging from the fact that the ion production is observed in triplet-triplet annihilation (the energy of the lowest triplet state of pyrene is 2.1 eV), the energy of production of molecular ions in tetrahydrofuran does not exceed 4.2 eV. The obtained values of the ionization cross section show that the probability of production of molecular ions by nonradiative deactivation of the higher excited states of pyrene with approximate energy 5 eV is quite high. The complete scheme of the process is shown in Fig. 3. The fact that the indicated singlet transitions are allowed, together with the large probability of the subsequent ionization, accounts for the high value of σ_s.

Such values of σ_s make it possible, in principle, to change the relative concentrations of the molecular ions and of the excited molecules by changing the intensity of the light. If these states are active centers that realize various chemical-reaction channels, then it is possible to obtain directed chemical transformations with the aid of lasers.

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CONCERNING AN EXPERIMENTAL VERIFICATION OF THE SELF-CONSISTENT POTENTIAL FOR 4f ELECTRONS OF RARE-EARTH ATOMS

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In the case of the 4f electrons in the rare-earth region, self-consistent calculations of many-electron atoms, performed within the framework of the Hartree [1], Hartree-Fock-Slater [2], and Dirac-Slater [3] methods, lead to effective potentials (self-consistent + centrifugal) with two minima (Fig. 1). These correspond to two possible states of the 4f electron, with nearly equal energies but with greatly differing (by an approximate factor of 20) mean radii (external and internal "collapsed" states [1]). This situation, which is curious in itself, explains many unusual properties of rare-earth metals, particularly the so called isomorphic phase transition in cerium. At the same time, although the models used to obtain the results

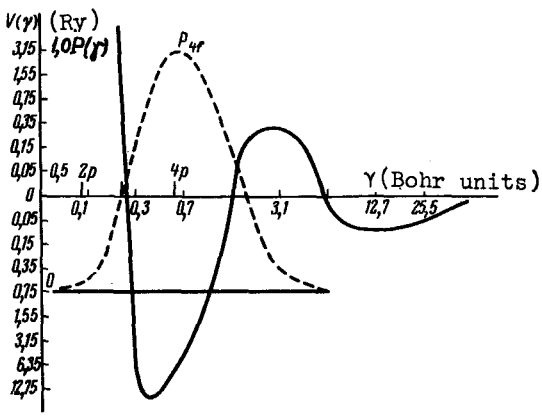

Fig. 1. Effective (self-consistent + centrifugal) potential for 4f electrons of Ce [2]. The 4f-electron radial wave function P_{4f} is also shown (dashed), as is the position of maxima P_{2p}, P_{3p}, P_{4p}. Attention should be called to the nonlinearity of the scale of the potential in both axes.

have been highly perfected, the situation calls for an experimental verification.

The usual verification by comparing the experimental and calculated binding energies (cf., e.g., [1]) obviously does not reflect uniquely, the radial distribution in the case of a potential with two minima, and cannot serve as a criterion for the presence of a "collapse."

A new experimental-verification method is afforded by the use of the effect of the chemical shift of x-ray lines, i.e., the change of their energy occurring when the valence configuration of the emitting atom is changed [4, 5]. The shift depends on the overlap of the wave function of the configuration-changing electron and the wave functions of the internal reference levels, the change of the energy spacing between which is being measured. The shift should be anomalously large when the valence configurations in the compared chemical compounds have different numbers of 4f electrons, if the f-electron "has collapsed," i.e., it occupies a deep radial position [5]. The possibility of measuring the shift for a number of K-series lines, namely $K_{\alpha 2}(1s_{1/2} - 2p_{1/2})$, $K_{\alpha 1}(1s_{1/2} - 2p_{3/2})$, $K_{\beta 3}(1s_{1/2} - 3p_{1/2})$, $K_{\beta 1}(1s_{1/2} - 3p_{3/2})$, $K_{\beta 2,4}(1s_{1/2} - 4p_{1/2,3/2})$, makes it possible to verify the course of the wave function of the 4f electron at several values of the radius, corresponding to the 2p, 3p, and 4p shells (see Fig. 1).

The expected shifts can be expressed in terms of the eigenvalues ε of the energy operator of the investigated self-consistent potential

$$\Delta E_{K\alpha_2} = (\varepsilon_{1s\,1/2} - \varepsilon_{2p\,1/2})_{4f^{n-1}} - (\varepsilon_{1s\,1/2} - \varepsilon_{2p\,1/2})_{4f^{n}}, \text{ etc.} \qquad (1)$$

The indices $4f^{n-1}$ and $4f^{n}$ reflect here the difference in the number of 4f electrons in the compared configurations.

The values of ΔE_K can be directly compared with the experimental ones.[1)]

The table and Fig. 2 (where the coordinates are E, the energy of the x-ray line, and ΔE, its chemical shift) show the shifts calculated from relations (1) using the eigenvalues

[1)] The fact that the Koopmans theorem [6] is not exactly satisfied in this case has apparently little significance, since the errors in the relation $E_K = \varepsilon_{1s} - \varepsilon_{Np}$ cancel out when a second similar difference, corresponding only to another valence configuration of the atom, is subtracted.

Comparison of theoretical and experimental shifts of K-series x-ray lines corresponding to removal of 4f electron in rare-earth atoms

Measured line	$\Delta E = E_{4f^{n-1}} - E_{4f^n}$, meV			
	Theory		Experiment	
	Herman and Skillman [2]	Waber [3]	This work *	
$K_{\alpha 2}(1s_{1/2} - 2p_{1/2})$	−626 ±70	−419.2	−582 ± 15	−464 ± 20
$K_{\alpha 1}(1s_{1/2} - 2p_{3/2})$	−694±70	−463.3	−643±15	−525 ±20
$K_{\beta 3}(1s_{1/2} - 3p_{1/2})$	−1973±70	–	−1725±55	−1640±60
$K_{\beta 1}(1s_{1/2} - 3p_{3/2})$	−1986±70	–	−1450±40	−1370±50
$K_{\beta 2,4}(1s_{1/2} - 4p_{1/2,3/2})$	−510±70	–	−300 ±60	−420 ± 70

*Before and after correction for 5d-electron shift

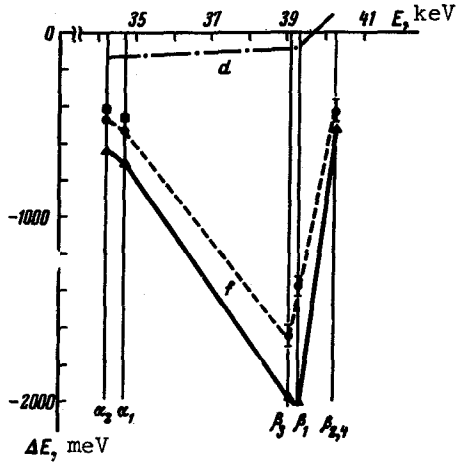

Fig. 2. Comparison of theoretical shifts of the K-series x-ray lines, calculated with the potential of Fig. 1, with the experimental ones. Triangles and squares - theoretical from data of [2] and [3] for Ce and Eu, respectively; circles - results of our measurements for EuF_2 - EuF_3, corrected for the shifts due to the 5d electrons (dash-dot curve in upper part of figure).

calculated by Herman and Skillman [2] for the configurations $4f^n6s^2$, $4f^{n-1}6s^25d^1$ of cerium and by Waber [3] for analogous europium configurations. The self-consistent Herman-Skillman potential and the corresponding wave function of the 4f electron are shown in Fig. 1. The table and Fig. 2 show also the experimental values obtained by us by applying the usual procedure (see [4, 5]) to samples of EuF_2 and EuF_3. The near-100% ionicity of the bond in these compounds allows us to regard europium as a doubly-charged and respectively triply-charged ion with configurations $...4f^7$ and $...4f^6$. Thus, the experimental shifts correspond to effects due to total removal of one 4f electron. The theoretically calculated effect, using the assumed configurations (see above), corresponds to removal of a 4f electron and addition of a 5d electron. The latter is of little importance, however, since the effect due to the d-electron (approximately plotted in Fig. 2 - dash-dot line) is much smaller than the effect from the f electron.

Notice should be taken of the anomalously large values of the effects from the 4f electron, which exceeds the usual ones [4, 5] by a factor 10 - 20. The theoretical and experimental quantities are in good agreement, and the characteristic form of the curve offers evidence in favor of the verified potential. The agreement is particularly accurate for the Waber's relativistic solution, which pertain directly to the experimentally investigated europium.

It should also be noted that the $\Delta E = \phi(E)$ relation can serve as a sui generis "facsimile" of the 4f electron, by which it is possible to identify experimentally events in which this electron takes part.[1)]

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ABSORPTION OF ULTRASOUND BY TIN IN THE INTERMEDIATE STATE

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Andreev has shown in a theoretical paper [1] that the absorption of high-frequency ultasound in a pure superconductor in the intermediate state, under condition when the normal-layer thickness a_n becomes comparable with the wavelength of sound, is described by the expression

$$\alpha/\alpha_n = \eta\Phi(2a_n/\lambda)$$

where α and α_n are the sound absorption coefficients in the intermediate and in the normal states, respectively, η is the concentration of the normal phase, and $\Phi(x)$ is a function that ranges from zero at $x = 0$ to unity when $x \to \infty$. Thus, it follows from this formula that the sound absorption should be smaller than η is $a_n \sim \lambda$. This behavior of the sound absorption coefficient is closely linked with the peculiar law governing the reflection of excitations incident on the interface between the normal and superconducting phases [2].

Measurements of α/α_n when the form of the function $\Phi(x)$ is known may serve as an indirect method of determining a_n and the period $d = a_n/\eta$ of the layered structure, in the

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[1)] A plot of $\Delta E = \phi(E)$ for d-electrons is shown in Fig. 2. The "facsimiles" of the s- and p-electrons in the region of the $K_{\alpha 1,2}$ and $K_{\beta 1,3}$ lines change the form of the horizontal lines located a height +80 and +100 meV. On the $K_{\beta 2,4}$ line, however, they become strongly bent, with the curve for the s-electron going downward (becoming negative), while that of the p-electron goes upward. We hope to discuss this in one of our future papers.