Coster-Kronig decay width of Rb

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3*p* Coster-Kronig decay of Rb($Z=37$) has been studied by comparing the new experimental and theoretical decay widths with earlier predictions and with the results for the neighboring atom Kr($Z=36$). The insensitivity of the Coster-Kronig single-channel transition rate around $Z=37$ to the choice of orbitals and transition energy has been discussed. The reliability of the intermediate-coupling calculations in determining the experimental Coster-Kronig level widths has been called into question.

I. INTRODUCTION

Recently we studied the 3*d* Auger spectrum of Rb ($Z=37$) in detail.[1] Final-state correlation effects were found to be of major importance in the spectra. In this work we will continue our study of Rb to the Coster-Kronig (CK) transitions. The main CK transitions of Rb have reasonable energies around 100 eV, which is why their study becomes fairly easy both experimentally and theoretically. Since the super CK decay becomes energetically forbidden in going from Kr ro Rb, the latter offers an ideal test case for CK level width predictions. This is why Rb has already been studied extensively in the past, both experimentally[2] and theoretically.[3–6] The 3*p* level widths around $Z=37$ were calculated by McGuire[3] and by Yin *et al.*[4] using the Hartree-Slater (HS) approach, and by Ohno and Wendin[5,6] using many-body perturbation theory and random-phase approximation with exchange (RPAE).

The theoretical CK rates have been calculated in this work by a single-channel Dirac-Fock (DF) Auger rate code that we have introduced recently.[7] The dependence of the transition rate on the choice of potential and transition energy has been examined. Our results have also been compared with earlier predictions[3–6] in order to further study the dependence of final results on the details of the calculation method. The coupling between various electron emission channels has not been taken into account in this work and needs to be studied separately.

Intermediate-coupling calculations were used by Menzel and Mehlhorn[2] to determine the experimental CK level width of Rb. They generated a set of theoretical peaks and intensities using McGuire's radial integrals. Then they found the Lorentzian linewidth that brought this spectrum into agreement with experiment. In the present work, the linewidth has been calculated *a priori*, so there is no fitting. A theoretical spectrum is then generated using the calculated linewidth and the line positions and intensities from relativistic intermediate-coupling calculations. Finally the theoretical profile is compared with experiment.

II. EXPERIMENT

The electron-beam-excited Auger spectrum of Rb was measured at the University of Oulu by means of a high-resolution cylindrical-mirror-type electron spectrometer.[8] The energy resolution of the analyzer was better than 0.1% and the spectra were measured without retardation.

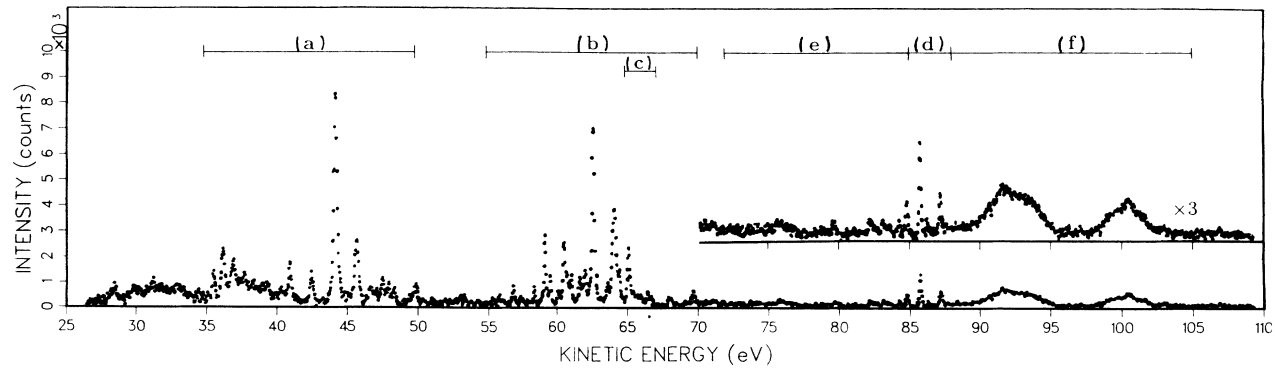

FIG. 1. Experimental $M_{4,5}$ Auger and $M_{2,3}$ Coster-Kronig spectra of Rb. (a)–(f) refer to the transitions in the following way: (a) $3d^9 \rightarrow 4s4p^5 5s$; (b) $3d^9 \rightarrow 4s^2 4p^4 5s$; (c) $3d^9 \rightarrow 4s4p^6$; (d) $3d^9 \rightarrow 4s^2 4p^5$; (e) $3p^5 \rightarrow 3d^9 4s4p^6 5s$; (f) $3p^5 \rightarrow 3d^9 4s^2 4p^5 5s$.

The primary beam energy was 2 keV and the beam current was typically 1 mA. Emitted Auger electrons are detected in this spectrometer at the mean emission angle of 54.5° with respect to primary electron beam. The atomic Rb vapor target was generated in a resistively heated oven. The vapor pressure inside the oven, where the Auger electrons were created by the through-going primary beam, was estimated to be about 10^{-4} torr. The energy calibration was done with the aid of the Kr *MNN* Auger spectrum.

The dispersion-corrected and background-subtracted spectrum is depicted in Fig. 1. The spectrum has been divided in sections (a)–(f) as follows:

$$\begin{aligned}
&\text{(a)}\ 3d^9 \rightarrow 4s4p^5 5s\ , \\
&\text{(b)}\ 3d^9 \rightarrow 4s^2 4p^4 5s\ , \\
&\text{(c)}\ 3d^9 \rightarrow 4s4p^6\ , \\
&\text{(d)}\ 3d^9 \rightarrow 4s^2 4p^5\ , \\
&\text{(e)}\ 3p^5 \rightarrow 3d^9 4s4p^6 5s\ , \\
&\text{(f)}\ 3p^5 \rightarrow 3d^9 4s^2 4p^5 5s\ .
\end{aligned} \tag{1}$$

The $3d$ Auger transitions (a)–(d) have been reported elsewhere[1] and are not discussed below. In this work we will concentrate on the CK transitions (e) and (f).

III. COSTER-KRONIG TRANSITIONS

In order to analyze the measured spectrum in detail, the energy levels for the initial and final ionic states of the decay processes were first computed using the MCDF code of Grant.[9] The results for $3d$ Auger transitions have been reported elsewhere.[1] For CK transitions (e) and (f) the energy-level diagram is shown in Fig. 2. The strongest primary transitions followed after ionization of $3p_{1/2,3/2}$ electrons are labeled by (a). Some of the resulting levels decay further by cascade transitions. The second step is indicated by (b) and the third step by (c) in Fig. 2.

The broad structures (e) and (f) at the kinetic energy region of 70–105 eV (Fig. 1) are due to the $3p$ CK transitions. In order to analyze the CK transitions in detail we first calculated the total transition rate of the line groups (e) and (f) and of the $3p^5 \rightarrow 3d^9 4s^2 4p^6$ transitions. The latter transitions fall outside our experimental spectrum (see Fig. 2) and their transition rate was found to be fairly small—for the $3p_{1/2}$ initial hole we obtained 0.02 eV. The total rates were 2.37 and 2.55 eV for the $3p_{1/2}$ and $3p_{3/2}$ transitions, respectively. These values were used to obtain the natural widths of the lines in the CK spectra since the $3p$ widths are almost entirely due to the CK transitions. The radiative transition rates are very small,[4] the Super-Coster-Kronig transitions are energetically forbidden for Rb (see Fig. 2), and the $3p$ and $3d$ Auger transition rates were found to be at least two decades lower than the CK transition rates.

A. $3p^5 \rightarrow 3d^9 4s^2 4p^5 5s$ transitions

The spectral structure of the transitions at 88–105 eV in group (f) was calculated by using the intermediate-

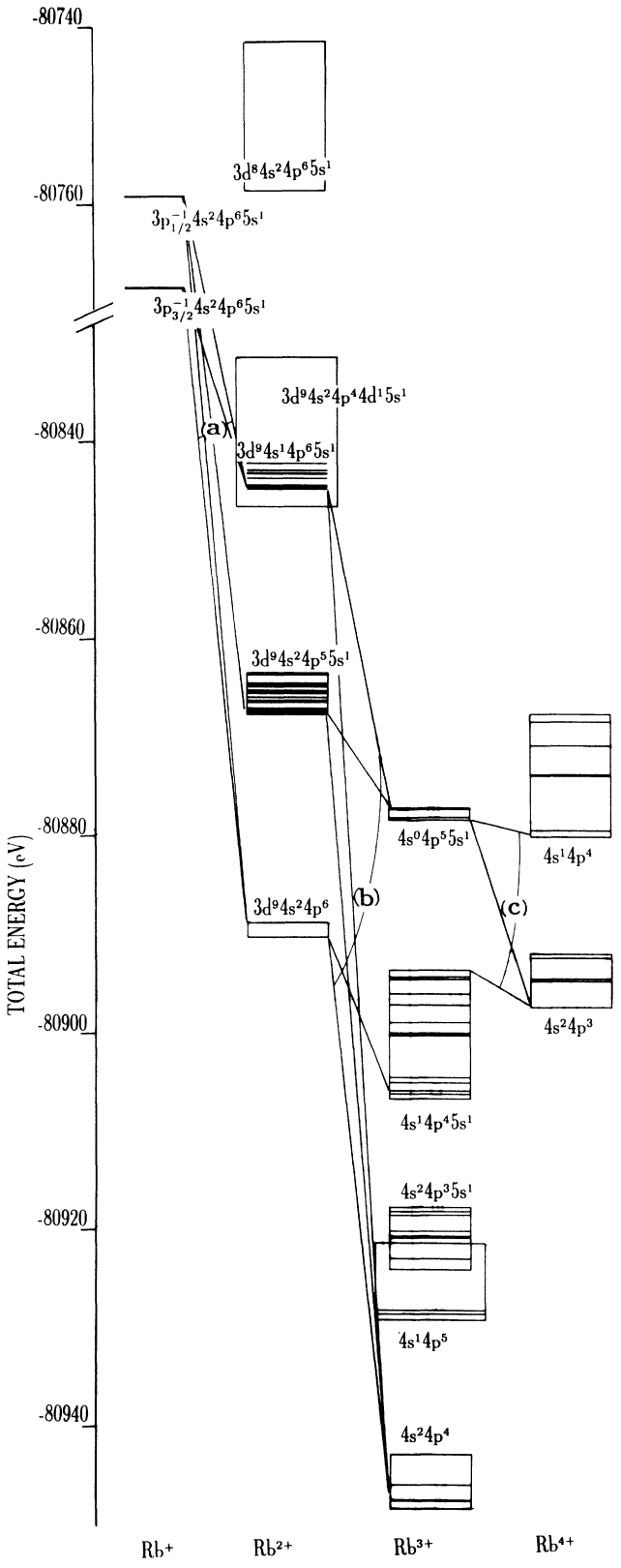

FIG. 2. Energy-level diagram of Rb computed using the MCDF code of Grant (Ref. 9). Channel *A* shows the first step transitions in filling the $3p$ vacancy, channel *B* the second step transitions, and channel *C* the third step transitions.

TABLE I. Dependence of the $3p_{1/2}^{-1} \rightarrow 3d^{-1}4p^{-1}$ CK decay rates of Rb on the Auger energy and on the potential where the wave functions have been calculated.

Wave function	Potential[a]	Transition rate (eV) Calc.[b]	Calc.[c]
Continuum	Rb^+		
		1.844[d]	1.936
Bound	Rb^+	1.653[e]	
Continuum	Rb^{2+}		
		1.588	1.664
Bound	Rb^+		
Continuum	Rb^{2+}		
		1.675	1.755
Bound	Rb^{2+}		
Continuum	Rb		
		1.657	1.734
Bound	Rb		

[a]Choice of the potential where the wave function has been calculated.
[b]With calculated transition energy.
[c]With experimental transition energy. Calculations b and c thus show the energy dependence of transition rates.
[d]Solid curve in Fig. 3 corresponds to this calculation. Note that all results agree within 20%, this one being one of the largest.
[e]DS orbitals. All the other values are from DF calculations.

coupling states for both the initial and final ionic configurations. The DF continuum orbitals used in the calculation of the transition rates were determined in the $3p$-hole-state potential and the DF bound orbitals were calculated for the $3p$-hole state. This effectively neglects the relaxation of the orbitals during the CK transitions.

The theoretical CK spectrum is compared in Fig. 3 with the corresponding experimental spectrum which is shifted by 4.8 eV towards higher energy to fit the calculated $3p_{3/2}$ peak maximum. This energy difference between experiment and theory is partly due to the strong coupling between the discrete initial and the continuum final states leading to modification of the energy of the initial hole state.[10] The spectrometer broadening is negligible in comparison with the natural width and was therefore omitted. The solid curve shows the calculated spectrum obtained as superposition of Lorentzians with theoretical widths of 2.37 eV ($3p_{1/2}$) and 2.55 eV ($3p_{3/2}$), respectively. The line positions correspond to the calculated transition energies and the relative heights are equal to the calculated transition rates. The dashed curve was obtained with the same line positions and heights but with widths of 0.85 eV ($3p_{1/2}$) and 1.15 eV ($3p_{3/2}$), respectively, which were obtained in Ref. 2 from the experimental spectrum. Comparison between experimental points and calculated profiles of Fig. 3 shows that the solid curve clearly overestimates but the dashed curve slightly underestimates the extent of the $3p_{3/2}$ and $3p_{1/2}$ CK groups.

In order to study the dependence of the CK rates on the transition energy and the ionic potential, we calculated the CK rates for group (f) using various bound and continuum orbitals (Table I). The DF result of 1.84 eV was obtained as discussed above. As can be seen from Table I, the rate is reduced by about 10% if the Dirac-Slater (DS) orbitals are used. The energy dependence of the rate was tested by reducing the calculated CK energy by 4.8 eV to correspond the experimental energy. As can be seen from Table I, different choices of the bound and

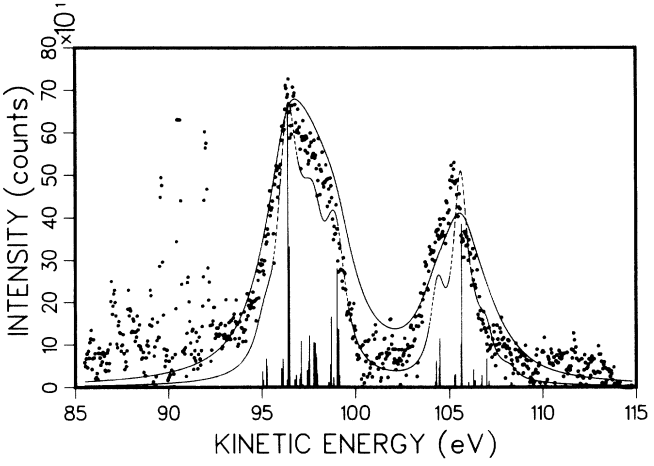

FIG. 3. The $3p^5 \rightarrow 3d^9 4s^2 4p^5 5s$ spectrum of Rb denoted by (f) in Fig. 1. Experimental spectrum, shifted by 4.8 eV to higher energy, is given by points. Vertical bars show the transition rates and their horizontal positions show the energies of individual multiplets predicted by intermediate-coupling calculations. Solid curve is the calculated spectrum obtained with widths of 2.37 (M_2) and 2.55 (M_3) eV (see footnote e of Table I), and dashed curve with widths (Ref. 2) of 0.85 (M_2) and 1.15 (M_3) eV.

TABLE II. The $3p_{1/2}^{-1} \rightarrow 3d^{-1}4p^{-1}$ CK decay rates of Kr.

	Transition rate (eV)
This work[a]	1.66
Yien *et al.*[b]	1.40
McGuire[c]	1.87
Ohno and Wendin[d]	0.7–1.0
Experiment[e]	1.80

[a]DF orbitals using the $3p$-hole-state potential.
[b]HS orbitals using the ground-state potential (Ref. 4).
[c]HS orbitals using the single-hole-state potential (Ref. 3).
[d]RPAE calculation (Refs. 5 and 6). The rate is estimated from the $3p$ decay width since the authors reported that the partial widths due to super CK and CK are comparable in size.
[e]Total $3p$ level width including CK, super CK and experimental contributions (Ref. 11).

continuum orbitals as well as energies lead to a variation in the transition rate that is less than 20% .

A further test for the sensitivity of CK rate to the details of the calculation can be obtained by comparing our results with earlier nonrelativistic calculations.[3–6] This is done in Table II for the neighboring element Kr ($Z=36$), for which more results[3–6] are available. Table II shows, somewhat surprisingly, fairly good agreement between our transition rate and those of Yien *et al.*[4] and McGuire.[3] The variation is not much larger than obtained above for Rb using different orbitals or energies. Only the RPAE prediction of Ohno and Wendin is smaller by about a factor of 2 than the others.

In Rb the widths of 1.15 and 0.85 eV for $3p_{3/2}$ and $3p_{1/2}$, respectively, determined by Menzel and Mehlhorn,[2] were reported to be in good agreement with the results of Ohno and Wendin.[5,6] The dashed line in Fig. 3, obtained using these line widths but our relative DF energies and intensities, does not, however, fully account for the experimental spread and shape of the Coster-Kronig line groups. This indicates that the fine structure reproduced by our relativistic intermediate-coupling calculations differs slightly from that generated by Menzel and Mehlhorn using nonrelativistic calculations. Detailed comparison with experiment is lacking since no fine structure is resolved. Therefore no conclusions from the validity of the calculations can be drawn. The intermediate-coupling calculations where the correlation effects, including the continuum interaction, are omitted may not, however, reproduce properly the energy splitting and intensity distribution of the fine-structure lines. The use of a calculated sum profile may therefore be inconclusive in the estimation of the natural width of individual lines. Our calculated profile (solid curve in Fig. 3) does not agree fully with experiment. In the case where the channel mixing would cause the disagreement, it would alter not only the decay width but also the intensity distribution of the fine structure.

B. $3p^5 \rightarrow 3d^9 4s 4p^6 5s$ transitions

A detailed study of the CK spectrum (e) around 72–85 eV is omitted in this work because of the low intensity, preventing a meaningful comparison between theory and experiment. The calculated decay rate for the group (e) transitions is 0.51 eV compared to the rate of 1.84 eV for the group (f) transitions. This is high enough that the spectrum could be detected. The final state of the decay (e), however, contains a $4s$ hole, which may cause strong electron correlation and redistribution of the intensity between several lines (see the results for the $3d$ Auger transitions in Ref. 1). Smearing out of a clear peak group is thus understandable.

IV. CONCLUSION

We obtained only minor changes in CK rates of Rb ($Z=37$) with the use of different DF orbitals. In spite of the DF calculations, the CK rate for Kr ($Z=36$) was not found to deviate considerably from the earlier nonrelativistic predictions of McGuire[3] and Yin *et al.*[4] The CK single channel rate is thus surprisingly insensitive to the details of the calculation. A deeper understanding of the finding needs to be sought. Only the results of Ohno and Wendin[5,6] deviate markedly from the other ones. The CK energies of Rb are not properly reproduced by DF calculations. The rate is fairly insensitive to the changes in energy ($E_k \sim 100$ eV), however. The next step is to study the importance of channel mixing. The intermediate-coupling calculations for open-shell atoms may not reproduce the fine structure of CK spectra properly, which is why they should be used with great caution in determining the experimental level widths. High-resolution photoelectron spectra are needed.

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