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ON THE EXISTENCE OF DIPOLE SATELLITES IN THE REGION OF $M_{2,3}$–$L_{2,3}$ NON-DIPOLE EMISSION LINES FOR TRANSITION ELEMENTS

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The reason of discrepancy between the experimental and the theoretical relative intensities of the 3p→2p electric quadrupole emission with respect to dipole 3s→2p emission for transition elements is investigated in relativistic configuration interaction approximation. The enhancement of theoretical intensity of quadrupole transitions by 4–6 times is obtained. It is shown that their relative intensity increases with the atomic number. In the single configuration approximation the dipole and the quadrupole transitions are separated in energy, but taking into account the configuration mixing their energy intervals extend and overlap. The dipole CI satellites with intensity exceeding the intensity of quadrupole transitions appear in their region, thus their separation becomes hardly possible.

Keywords: non-dipole emission, transition elements, intensities of lines

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1. Introduction

Using a high efficiency X-ray spectrometer it becomes possible to observe the electric quadrupole emission in the soft X-ray and the extreme ultraviolet region. Recently the transitions 3d→2s were registered for the first time in Sm, Ho, Yb [1] and their regularities were investigated theoretically for all lanthanides [2]. In [3] at the resonant and non-resonant production of $2p^{-1}$ vacancy the weak emission on the high energy side of 3s→2p lines was observed for three transition metals Co, Ni, and Cu. On the grounds of correspondence of this structure to the energy interval of 3p →2p transitions, these maxima were attributed to the electric quadrupole emission. Their total intensity relative to 3s→2p constitutes 1–5%. However, this quantity calculated for a free ion in non-relativistic single-configuration approximation was obtained 20–30 times smaller than its registered value. Two possibilities were suggested for the explanation of such discrepancy [3]. In the mechanism having a solid-state origin such transitions could be caused by symmetry breaking and vibronic coupling of $3d^{-1}$ vacancy state with $3p^{-1}$ state. However, the same relative intensity was obtained for emission of metallic Cu and CuO with a very different crystal structure. Thus the other possibility seemed more preferable, that enhancement of intensity of quadrupole emission had the atomic origin, correlation and relativistic effects. It has been supposed that they modify the 3p radial orbital so its overlap with 2p orbital essentially increases.

The aim of this work was to investigate the total intensities of quadrupole 3p →2p and dipole 3s→2p emission in transition elements using the large scale relativistic configuration interaction (CI) calculations for free atoms. In Sec. 2 the explicit approximate expression for the ratio of total intensities of quadrupole and dipole transitions is derived that enables one to determine the dependence of the ratio on atomic number. The results of the detailed calculations of spectra for the four elements from the end and beginning of the transition group are presented and discussed in Sec. 3.

2. Ratio of the total intensities of quadrupole and dipole transitions

In a general case the intensities of radiative transitions in atoms with open shells depend on the populations of excited levels. Taking into account that the emission spectra registered in [3] have been excited with monochromatic X-ray photons with the energy

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above L_2 ionization limit, the total intensity of spectrum corresponding to the considered transitions is expressed as follows:

$$I(K-K') = \sum_{\gamma\gamma'} I(K\gamma - K'\gamma')$$

$$= \sum_{\gamma} \frac{\sigma_{\rm ion}(K_0\gamma_0 - K\gamma)}{\Gamma(K\gamma)} \sum_{\gamma'} A(K\gamma - K'\gamma')\,, \quad (1)$$

where K_0 is the normal configuration and γ_0 is its ground state, $\sigma_{\rm ion}$ is the photoionization cross-section, Γ is the natural width of excited level, and A denotes the rate of radiative transition.

In Eq. (1) only the transition rate depends on many-electron quantum numbers γ' of the final state. This gives one the possibility to derive an approximate explicit expression for the ratio of total intensities under the assumption that the transition energy in the expression for the rate can be approximated by the average energy. Such substitution is reasonable, because the energies of dipole and quadrupole transitions are considerably higher than the energy interval of transition array. Then the summation over γ' is acting only on line strength. If the initial and the final configurations contain only one open active shell, summation can be performed algebraically in single configuration approximation [4]. The result does not depend on many-electron quantum numbers of the initial configuration:

$$\frac{1}{2J+1} \sum_{\gamma' J'} S_t\big(n_1 l_1^{4l_1+1} n_2 l_2^{4l_2+2} n_3 l_3^{N_3} \gamma J,$$
$$n_1 l_1^{4l_1+2} n_2 l_2^{4l_2+1} n_3 l_3^{N_3} \gamma' J'\big)$$
$$= \frac{1}{2l_1+1} \, \langle l_2 \| C^{(t)} \| l_1 \rangle^2 \langle n_2 l_2 | r^t | n_1 l_1 \rangle \,. \quad (2)$$

Here J is the total quantum number of the initial state. The second multiplier on the right-hand side is the submatrix element of the spherical function and the last multiplier is the radial integral of electric dipole ($t = 1$) or quadrupole ($t = 2$) transitions.

The 3p→2p and 3s→2p transitions begin from the same initial configuration with $2p^{-1}$ vacancy. Consequently the quantities $\sigma_{\rm ion}$ and $\Gamma(K\gamma)$ cancel out making the ratio of the total intensities of these transitions independent of the approximation used for their calculation. Thus this ratio equals the ratio of total transition rates:

$$\frac{I(3p-2p)}{I(3s-2p)} = \frac{A(3p-2p)}{A(3s-2p)}\,. \quad (3)$$

It is necessary to note that Eq. (2) is violated in CI approximation, if there appear line strengths of transitions between some mixing configurations, which do not obey the (2) summation rule.

Substitution of expressions for the total transition rates in terms of average energies and transition integrals into Eq. (3) gives

$$\frac{I(3p-2p)}{I(3s-2p)} = \frac{3\alpha^2}{50} \frac{E_{\rm av}(3p-2p)^5}{E_{\rm av}(3s-2p)^3} \frac{\langle 3p|r^2|2p\rangle^2}{\langle 3s|r|2p\rangle^2}\,. \quad (4)$$

Thus the ratio of total intensities does not depend explicitly on the number of electrons in the passive $3d^N$ shell. The variation of this ratio in the transition group will be considered in the following section on the grounds of calculation results for the average energies and radial integrals.

3. Results of calculations and their discussion

Calculations in various approximations were performed for three elements Co, Ni, and Cu from the end of the transition group, for which the weak 3p–2p lines had been registered, and for one element Ti from the beginning of this group in which case these transitions had not been detected. As in [3], the free ions missing two or a single 4s electron, present in the ground configuration, were considered.

It is useful to begin the consideration of the ratio of total intensities from the simple single-configuration quasirelativistic approximation. The values of the average transition energies and radial integrals for considered elements, calculated using Cowan code [5], are given in Table 1. The absolute values of radial integrals decrease with increasing atomic number, but their

Table 1. Average energies and radial integrals for 3s→2p and 3p→2p transitions.

Element, $3d^N$ shell	Radial integrals (in a. u.) $\langle 2p\|r\|3s\rangle$	$\langle 2p\|r^2\|3p\rangle$	Ratio of integrals $\frac{\|\langle 2p\|r^2\|3p\rangle\|}{\langle 2p\|r\|3s\rangle}$	Average transition energies (in eV) $\bar{E}$(3s–2p)	$\bar{E}$(3p–2p)
Ti, $3d^2$	0.08134	−0.08356	1.0273	394.3	424.0
Co, $3d^7$	0.05924	−0.05016	0.8467	680.3	723.1
Ni, $3d^8$	0.05622	−0.04595	0.8174	746.3	792.0
Cu, $3d^{10}$	0.05326	−0.04197	0.7880	813.9	862.0

Table 2. Ratio of total intensities of electric quadrupole 3p→2p and dipole 3s→2p transitions.

Element	Experiment [3]	I(3p–2p)/I(3s–2p)				
		Single configuration approximation				Relativistic CI
		quasirelativistic			relativistic	
		[3]	This work	Eq. (4)		
Ti	–	0.0003	0.0010	0.0010	0.0011	–
Co	0.012(1)	0.0007	0.0019	0.0019	0.0022	0.0039
Ni	0.022(1)	0.0009	0.0022	0.0022	0.0024	0.0053
Cu	0.050(3)	0.0016	0.0024	0.0024	0.0026	0.0062

ratio is diminished by one third while passing from Ti to Cu. The average energies increase for both transitions about twice. Consequently, the variation of the ratio of total transition rates for quadrupole and dipole transitions mainly depends on the higher power of transition energy contained in the rate for non-dipole transitions. That tendency corresponds to the registered diminishing of the ratio with decreasing Z, and the nondetection of quadrupole transitions for the elements of the first half of transition period.

The detailed calculation of spectra in the quasirelativistic single-configuration approximation gives the values of the total intensities ratio (Table 2) practically coinciding with those obtained from Eq. (4). However, this result is 3.3–1.5 times greater than presented in [3] using the same approximation. Also, the calculation in single configuration relativistic approximation has been performed by us with the GRASP software [6]. Fair agreement of all three results can be treated as their sufficient control. The difference between the values of ratio calculated in single-configuration approximation [3] and experiment is diminished by our calculation for about several times. However, the inconsistency by 6–8 times for Co, Ni and even about 20 times for Cu remains.

The next step was the application of relativistic CI approximation.

The set of configurations in CI expansion has been selected using the configuration interaction strength [7, 8]:

$$T(K,K') = \frac{\sum\limits_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle^2}{\bar{E}(K,K')^2}\,, \qquad (5)$$

where the quantity in the numerator is the interconfiguration matrix element of the Hamiltonian H and $\bar{E}(K,K')$ is the energy distance between the interacting levels of configurations K and K':

$$\bar{E}(K,K') = \Big\{ \sum_{\gamma\gamma'} \big[\langle K\gamma|H|K\gamma\rangle - \langle K'\gamma'|H|K'\gamma'\rangle\big] \times \langle K\gamma|H|K'\gamma'\rangle^2 \Big\} \Big[\sum_{\gamma\gamma'} \langle K\gamma|H|K'\gamma'\rangle^2\Big]^{-1}. \qquad (6)$$

The summation in (5) and (6) is performed over all states γ and γ' of both configurations.

This measure of configuration interaction has been calculated in relativistic approximation and 7–13 nl-configurations having the largest values of this measure have been selected. The mixing of all relativistic configurations corresponding to various distributions of electrons in the subshells of open shells has been included. The calculations of energy and emission spectra have been performed employing relativistic Flexible Atomic Code [9] using Dirac–Fock–Slater wavefunctions.

The following sets of configurations for the states of Co with $2p^{-1}$, $3s^{-1}$, and $3p^{-1}$ vacancies have been used (the closed shells are not indicated):

$$\begin{aligned} &2p^5 3d^7 + 2p^5 3d^6 (4s + 4d + 5d + 6d + 7d) \\ &\quad + 2p^5 3p^5 3d^7 (4p + 5p) + 2p^5 3s 3d^7 4s\,, \end{aligned} \qquad (7)$$

$$\begin{aligned} &3s3d^7 + 3d^6 + 3p^5 3d^6 (4f + 5f + 6f) \\ &\quad + [3s3d^6 + 3d^5](4d + 5d + 6d) \\ &\quad + 3s3p^5 3d^7 4p + 3p^4 3d^8\,, \end{aligned} \qquad (8)$$

$$\begin{aligned} &3p^5 3d^7 + 3p^5 3d^6 (4s + 4d + 5d + 6d + 7d) \\ &\quad + 3p^4 3d^7 4p\,. \end{aligned} \qquad (9)$$

Similar sets of configurations have been used for the Ni and Cu.

Inclusion of correlations among electrons increases the relative intensities of quadrupole transitions in free ions by about 1.5–2.5 times, but they remain 4–8 times smaller than the experimental values measured for metals. However, due to configuration mixing the intervals of both type transitions become wider and they are not separated from each other, as it has been in single configuration approximation. In Fig. 1 the calculated spectra of dipole and quadrupole transitions as well as the experimental spectrum are shown for Co.

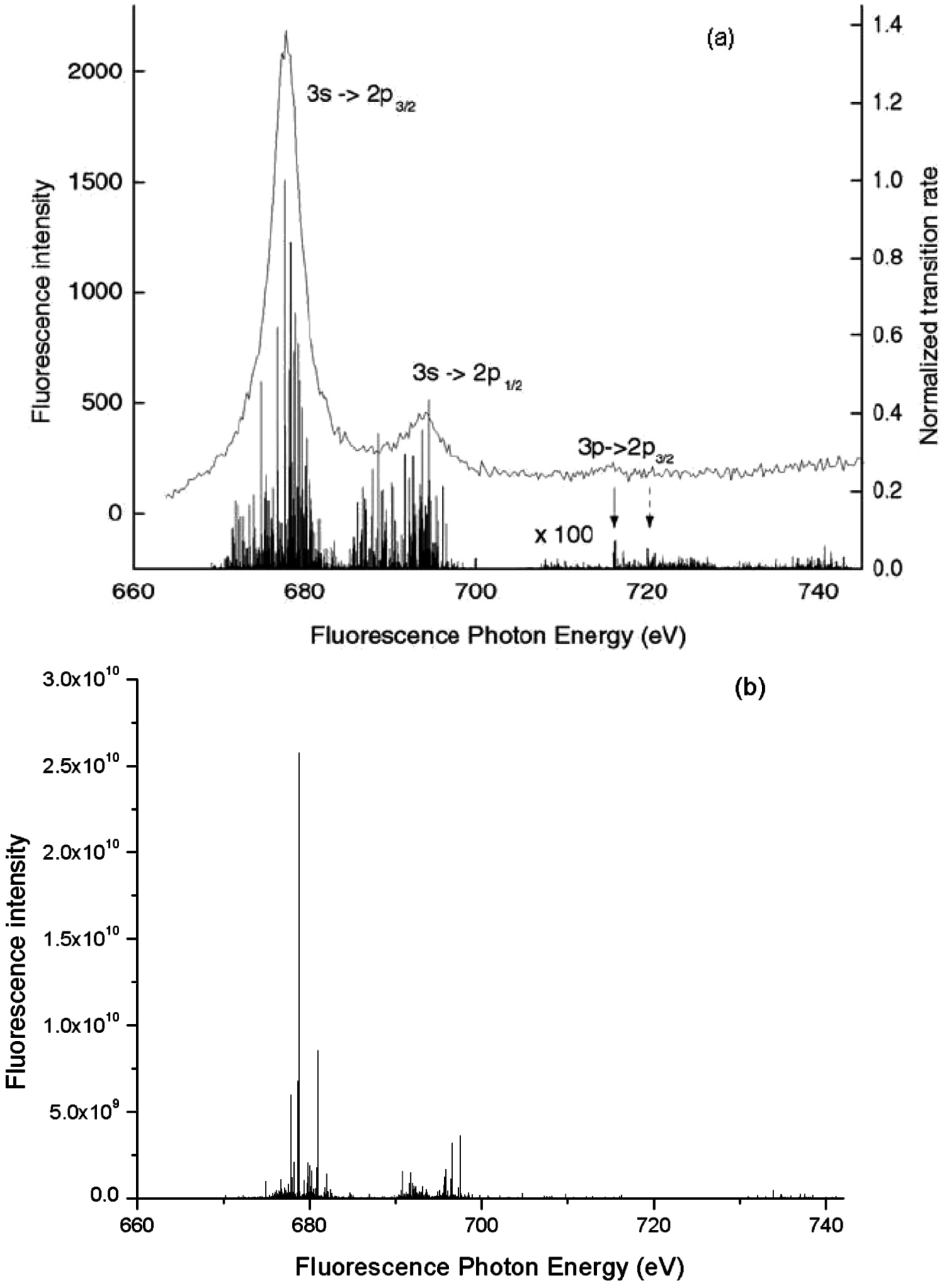

Fig. 1. Electric dipole 3s→2p and quadrupole 3p→2p emission in Co: (a) experiment and calculation in single configuration quasirelativistic approximation, reproduced with permission from [3], (b) calculation in relativistic CI approximation. The energy scales of all theoretical spectra are shifted to make the position of the main dipole maximum coincide with its observed position.

All theoretical spectrum is shifted by 9.8 eV to the higher energies in order to coincide the position of the line with maximum transition rate with the position of observed peak. The intensities of quadrupole transitions practically are not distinguished in the calculated spectrum. Many dipole satellite lines having considerably higher intensity than the quadrupole lines appear within their energy interval (Fig. 1(c, d)). One CI satellite group is situated at the high energy wing of transitions $2p_{3/2}$–3s, the most intense lines of this group correspond to the transitions $2p^5 3p^6 3d^7 \rightarrow 2p^6 3p^5 3d^6 4p^1$. The second group at 730–740 eV corresponds mainly to the two-electron transitions $2p^5 3d^7 \rightarrow 2p^6 3d^5 (5d+6d)$.

Similar results have been obtained for Ni and Cu. The energy positions of the main dipole CI satellites do not correspond to the maxima in the experimental spectra, attributed to quadrupole transitions.

If the intensity of dipole CI satellite lines were added to the essentially lower total intensity of quadrupole lines, the qualitative agreement of intensity ratio with

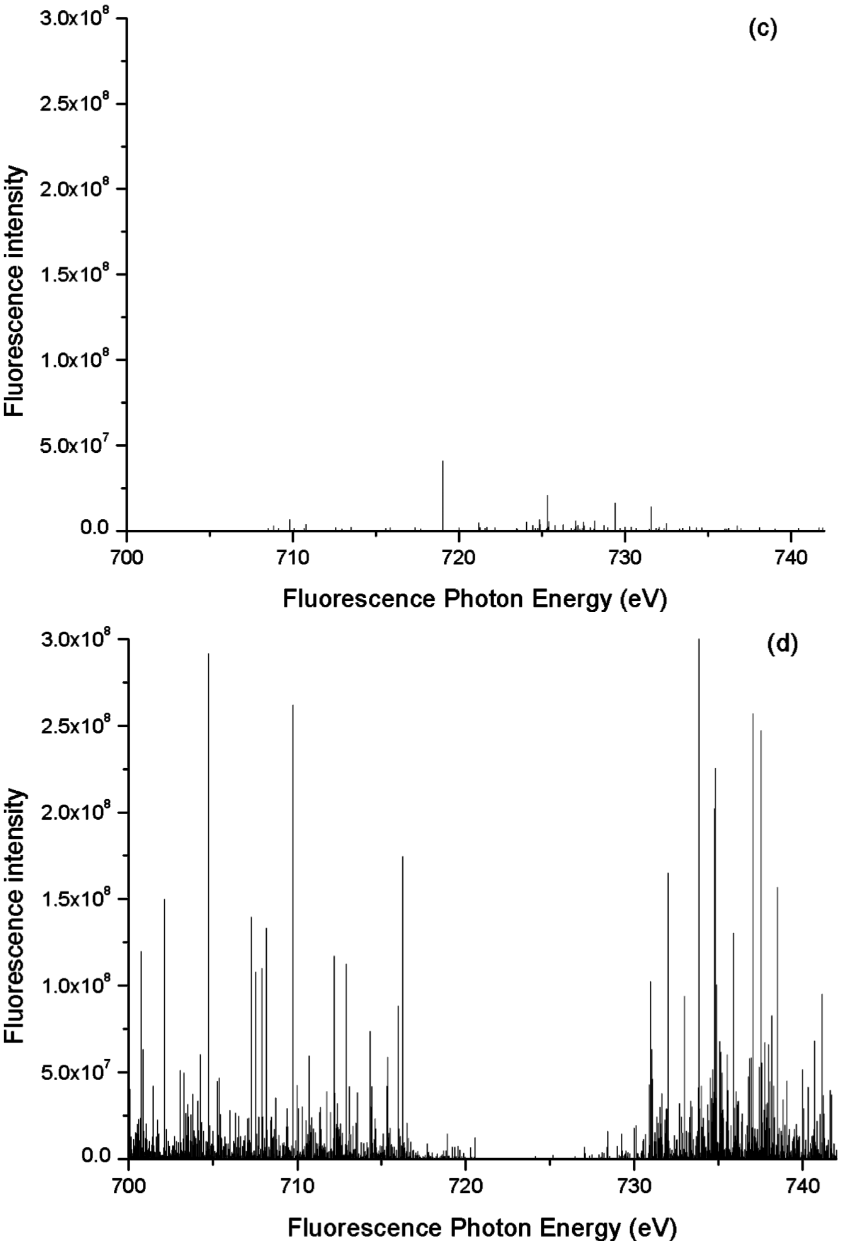

Fig. 1 (continued). Electric dipole 3s→2p and quadrupole 3p→2p emission in Co: (c) quadrupole transitions in CI approximation, (d) dipole transitions in the energy interval of quadrupole spectrum (relativistic CI approximation). The energy scales of all theoretical spectra are shifted to make the position of the main dipole maximum coincide with its observed position.

the experimental data can be obtained. However, there is no unambiguous way to determine the energy interval of the joint quadrupole plus dipole satellite lines array and to separate dipole transitions into the main and satellite groups. Due to the high density of CI dipole satellites for Co and Ni their separate lines are not distinguished in the experimental spectrum, but in such energy region the increase of the intensity takes place.

4. Conclusions

The large discrepancy between the experimental and the calculated relative intensity of quadrupole transitions obtained in [3] can be diminished by 2–3 times even in single configuration approximation using the quasirelativistic and relativistic methods. The same result follows from the obtained explicit formula. This formula has also been used to explain the reduction of the ratio of total intensities with the atomic number decrease. In single configuration approximation this ratio even in the presence of outer open shell does not depend on the populations of initial levels. However, such dependence appears in configuration interaction approximation, if the line strengths of transitions between some mixed configurations do not obey a simple summation rule.

In order to remove the remaining discrepancy with experiment, relativistic configuration interaction calculations have been performed. The sets of configurations for $2p^{-1}$, $3s^{-1}$, and $3p^{-1}$ vacancies included 7–11 nl-configurations selected using the approximate measure of configuration interaction between two configurations – the CI strength. Due to configuration mixing the additional dipole lines, exceeding in intensity the quadrupole lines, appear in the same energy interval. However, their energy positions do not correspond to the maxima in the experimental spectra attributed to quadrupole transitions, probably because of solid-state effects becoming important for the admixed excited configurations.

This consideration shows that configuration mixing can essentially extend the energy interval of emission spectrum and then any separation of total intensities of two overlapping spectra, especially of different intensity, becomes practically impossible.

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DIPOLINIŲ SATELITŲ EGZISTAVIMAS $M_{2,3}$–$L_{2,3}$ NEDIPOLINĖS EMISIJOS LINIJŲ SRITYJE GELEŽIES GRUPĖS ELEMENTUOSE

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Santrauka

Naudojantis didelės skiriamosios gebos Rentgeno spindulių spektrometru šalia elektrinių dipolinių šuolių 3s→2p linijų trijų geležies grupės metalų – Co, Ni ir Cu – spektruose buvo pastebėtos silpnos linijos, kurios pagal jų energijos vertes buvo priskirtos 3p→2p elektriniams kvadrupoliniams šuoliams. Tačiau jų santykinis intensyvumas, apskaičiuotas naudojantis laisvojo atomo modeliu vienkonfigūraciniu artutinumu, gautas 20–30 kartų mažesnis negu eksperimentinis. Vietoj vario ištyrus kitą kristalinę gardelę turintį vario oksidą, satelitinių linijų intensyvumas nepasikeitė, todėl padaryta išvada, kad teorijos nesutapimą su eksperimentu lemia koreliaciniai ir reliatyvistiniai efektai, į kuriuos nebuvo atsižvelgta atliekant skaičiavimus laisviesiems atomams.

Šiame darbe reliatyvistiniu konfigūracijų sumaišymo metodu, naudojantis didele banginių funkcijų baze, atlikti kvadrupolinių 3p–2p ir dipolinių 3s–2p šuolių intensyvumų skaičiavimai keturiems geležies grupės elementams – ir tiems, kuriems satelitinės linijos buvo stebėtos, ir Sc, kuriam jos nebuvo aptiktos. Parodyta, kad, atsižvelgus į konfigūracijų sumaišymą, kvadrupolinių linijų srityje atsiranda už juos intensyvesnės dipolinės linijos. Tačiau dviejų įvairaus intensyvumo persiklojančių spektrų, kurių linijos turi gana didelį natūralų plotį, išskyrimas yra beveik neįmanomas.