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**SENSING THE AUGER SPECTRA FOR SOLIDS:
NEW QUANTUM APPROACH
(За матеріалами доповіді на конференції СЕМСТ-2)**

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Abstract

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It is proposed new approach to sensing Auger spectra of solids and calculation of characteristics of Auger decay within S-matrix Gell-Mann and Low formalism. The energies of Auger electron transitions in solids (Na,Si,Ge,Ag) are calculated with account for correlation effects.

Key words: sensing Auger spectra, solids, quantum calculation

Резюме

ДЕТЕКТУВАННЯ ОЖЕ СПЕКТРІВ ТВЕРДИХ ТІЛ: НОВИЙ КВАНТОВИЙ ПІДХІД

С. В. Амбросов, А. В. Глушков, Л. В. Нікола

Розвинуто новий підхід до детектування Оже-спектрів твердих тіл та розрахунку характеристик Оже розпаду в межах S-матричного формалізму Гелл-Мана та Лоу. З урахуванням кореляційних ефектів розраховані енергії Оже переходів у Na,Si,Ge,Ag.

Ключові слова: детектування Оже спектрів, тверді тела, квантовий розрахунок

Резюме

ДЕТЕКТИРОВАНИЕ ОЖЕ СПЕКТРОВ ТВЕРДЫХ ТЕЛ: НОВЫЙ КВАНТОВЫЙ ПОДХОД

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Развит новый подход к детектированию Оже спектров твердых тел и расчету характеристик Оже распада в рамках S-матричного формализма Гелл-Мана и Лоу. С учетом корреляционных эффектов рассчитаны энергии Оже переходов в Na,Si,Ge,Ag.

Ключевые слова: детектирование Оже спектров, твердые тела, квантовый расчет

Introduction

The Auger electron spectroscopy is an effective method to study the chemical composition of solid surfaces and near-surface layers [1-8]. Sensing the Auger spectra in atomic systems and solids gives the

important data for the whole number of scientific and technological applications. When considering the method principles, the main attention is given as a rule to the models for drawing chemical information from the Auger spectra and to the surface

composition determination methods by the Auger spectrum decoding. It is just the two-step model that is used most widely when calculating the Auger decay characteristics. Since the vacancy lifetime in an inner atomic shell is rather long (about 10^{-17} to 10^{-14} s), the atom ionization and the Auger emission are considered to be two independent processes. In the more correct dynamic theory of the Auger effect [1-4] the processes are not believed to be independent from one another. The fact is taken into account that the relaxation processes due to Coulomb interaction between electrons and resulting in the electron distribution in the vacancy field have no time to be over prior to the transition. In fact, a consistent Auger decay theory has to take into account correctly a number of correlation effects, including the energy dependence of the vacancy mass operator, the continuum pressure, spreading of the initial state over a set of configurations etc. [1-6]. Note that the effects are not described adequately to date, in particular within the Auger decay theory [2]. In this paper a new approach to detection of the Auger decay characteristics for complex atomic systems basing on the S-matrix formalism by Gell-Mann and Low [7-15] is used for sensing the Auger spectra of solids and calculation of its characteristics. The novel element consists in an using the optimal basis of the electron state functions derived from the condition that the calibration-non-invariant contribution of the second order polarization diagrams to the imaginary part of the multi-electron system energy is minimized already at the first non-disappearing approximation of the perturbation theory (PT) [10, 11, 15]. Earlier the method has been applied to calculate the ionization cross-sections of inner shells in various atoms and quasimolecules (c.f.[8, 10]).

Method for calculating the line intensities and widths in the Auger spectra

Within the frame of QED PT approach [8-11] to the Auger effect description, the Auger transition probability and, accordingly, the Auger line intensity are defined by the square of an electron interaction matrix element having the form:

$$V_{1234}^{\omega} = [(j_1)(j_2)(j_3)(j_4)]^{1/2} \times \sum_{\lambda\mu} (-1)^{\mu} \begin{pmatrix} j_1 j_3 & \lambda \\ m_1 - m_3 & \mu \end{pmatrix} \times \text{Re} Q_{\lambda}(1234);$$

$$Q_{\lambda} = Q_{\lambda}^{\text{Qu}} + Q_{\lambda}^{\text{Br}}. \quad (1)$$

The terms Q_{λ}^{Qu} and Q_{λ}^{Br} correspond to subdivision of the potential into Coulomb part $\cos|\omega|r_{12}/r_{12}$ and Breat one, $\cos|\omega|r_{12}\alpha_1\alpha_2/r_{12}$. The real part of the electron interaction matrix element is determined using expansion in terms of Bessel functions: :

$$\frac{\cos|\omega|r_{12}}{r_{12}} = \frac{\pi}{2\sqrt{r_1 r_2}} \times \sum_{\lambda=0}^{\infty} (\lambda) J_{\lambda+1/2}(|\omega|r_{<}) J_{-\lambda-1/2}(|\omega|r_{>}) P_{\lambda}(\cos \mathbf{r}_1 \mathbf{r}_2). \quad (2)$$

where J is the 1st order Bessel function, $(\Lambda)=2\Lambda+1$. The Coulomb part Q_{λ}^{Qu} is expressed in terms of radial integrals R_{Λ} , angular coefficients S_{Λ} [9]:

$$\text{Re} Q_{\lambda}^{\text{Qu}} = \frac{1}{Z} \text{Re} \{ R_{\lambda}(1243) S_{\lambda}(1243) + R_{\lambda}(\tilde{1}24\tilde{3}) S_{\lambda}(\tilde{1}24\tilde{3}) + R_{\lambda}(1\tilde{2}\tilde{4}3) S_{\lambda}(1\tilde{2}\tilde{4}3) + R_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) S_{\lambda}(\tilde{1}\tilde{2}\tilde{4}\tilde{3}) \}. \quad (3)$$

As a result, the Auger decay probability is expressed in terms of $\text{Re} Q_{\Lambda}(1243)$ matrix elements:

$$\text{Re} R_{\lambda}(1243) = \iint dr_1 r_1^2 r_2^2 f_1(r_1) f_3(r_1) \times f_2(r_2) f_4(r_2) Z_{\lambda}^{(1)}(r_{<}) Z_{\lambda}^{(1)}(r_{>}). \quad (4)$$

where f is the large component of radial part of single electron state Dirac function; function Z is :


$$Z_{\lambda}^{(1)} = \left[\frac{2}{|\omega_{13}| \alpha Z} \right]^{\lambda+1/2} \frac{J_{\lambda+1/2}(\alpha|\omega_{13}|r)}{r^{\lambda} \Gamma(\lambda + 3/2)}.$$

The angular coefficient is defined by standard way [7]. The other items in (3) include small components of the Dirac functions; the sign “~” means that in (3) the large radial component f_i is to be changed by the small g_i one and the moment l_i is to be changed by $\tilde{l}_i = l_i - 1$ for Dirac number $\kappa_i > 0$ and $l_i + 1$ for $\kappa_i < 0$. The Breat interaction is known to change considerably the Auger decay dynamics in some cases (c.f. [9]). The Breat part of Q is defined as the sum:

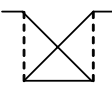
$$Q_{\lambda}^{\text{Br}} = Q_{\lambda, \lambda-1}^{\text{Br}} + Q_{\lambda, \lambda}^{\text{Br}} + Q_{\lambda, \lambda+1}^{\text{Br}}, \quad (5)$$

where the contribution of our interest is determined as:

$$Q_{\lambda}^{\text{Br}} = \frac{1}{Z} \text{Re} \{ R_{\lambda}(12\tilde{4}\tilde{3}) S'_{\lambda}(12\tilde{4}\tilde{3}) + R_{\lambda}(\tilde{1}\tilde{2}43) S'_{\lambda}(1243) + R_{\lambda}(\tilde{1}\tilde{2}\tilde{4}3) S'_{\lambda}(\tilde{1}\tilde{2}\tilde{4}3) + R_{\lambda}(1\tilde{2}\tilde{4}\tilde{3}) S'_{\lambda}(1\tilde{2}\tilde{4}\tilde{3}) \}. \quad (6)$$

The Auger width is obtained from the adiabatic Gell-Mann and Low formula for the energy shift [10]. The contribution of the $A_d =$  diagram to the Auger level width with a vacancy $n_\alpha l_\alpha j_\alpha m_\alpha$ is:

$$\sum_{\lambda} \frac{2}{(\lambda)(j_\alpha)} \sum_{\beta\gamma \leq f} \sum_{k>f} Q_{\lambda}(\alpha k \gamma \beta) Q_{\lambda}(\beta \gamma k \alpha), \quad (7)$$

while contribution of the $A_{ex} =$  one is:

$$\frac{2}{(j_\alpha)} \sum_{\lambda_1 \lambda_2} \sum_{\beta\gamma \leq f} \sum_{k>f} Q_{\lambda_1}(\alpha k \gamma \beta) Q_{\lambda_2} \times (\beta \gamma k \alpha) \begin{Bmatrix} j_\alpha & j_\gamma & \lambda_2 \\ j_k & j_\beta & \lambda_1 \end{Bmatrix}. \quad (8)$$

The formulas (7),(8) define the full Auger level width. The partial items of the $\sum_{\beta\gamma} \sum_k$ sum answer to contributions of $\alpha^{-1} \rightarrow (\beta\gamma)^{-1} K$ channels resulting in formation of two new vacancies $\beta\gamma$ and one free electron k : $\omega_k = \omega_\alpha + \omega_\beta - \omega_\alpha$. The final expression for the width in the representation of jj-coupling scheme of single-electron moments has the form:

$$\Gamma(2j_1^o l_1^o, 2j_2^o l_2^o; J) = 2 \sum_{j_k l_k} |\Gamma(2j_1^o l_1^o, 2j_2^o l_2^o; l_o, k j l)|^2 \quad (9)$$

Here the summation is made over all possible decay channels. The basis of electron state functions was defined by the solution of Dirac equation (integrated numerically using the Runge-Cutt method). The calculation of radial integrals $\mathbf{Re}R_\lambda(1243)$ is reduced to the solution of a system of differential equations [9]:

$$\begin{aligned} y_1' &= f_1 f_3 Z_\lambda^{(1)}(\alpha|\omega|r) r^{2+\lambda} \\ y_2' &= f_2 f_4 Z_\lambda^{(1)}(\alpha|\omega|r) r^{2+\lambda} \\ y_3' &= [y_1 f_2 f_4 + y_2 f_1 f_3] Z_\lambda^{(2)}(\alpha|\omega|r) r^{1-\lambda} \end{aligned} \quad (10)$$

In addition, $y_3(\infty) = \mathbf{Re}R_\lambda(1243)$, $y_1(\infty) = X_\lambda(13)$. The system of differential equations includes also equations for functions $f/r^{|\kappa|-1}$, $g/r^{|\kappa|-1}$, $Z_\lambda^{(1)}$, $Z_\lambda^{(2)}$. The formulas for the Auger decay probability include the radial integrals $R_\alpha(\alpha k \gamma \beta)$, where one of the functions describes electron in the continuum state. When calculating this integral, the correct normalization of the function Ψ_k is a problem. The correctly normalized function should have the following asymptotic at $r \rightarrow 0$

$$\left. \begin{matrix} f \\ g \end{matrix} \right\} \rightarrow (\lambda\omega)^{-1/2} \begin{cases} [\omega + (\alpha Z)^{-2}]^{-1/2} \sin(kr + \delta), \\ [\omega - (\alpha Z)^{-2}]^{-1/2} \cos(kr + \delta). \end{cases} \quad (11)$$

When integrating the master system, the function is calculated simultaneously:

$$\begin{aligned} N(r) &= \left\{ \omega_k \left[f_k^2 \left[\omega_k + (\alpha Z)^{-2} \right] + \right. \right. \\ &\quad \left. \left. + g_k^2 \left[\omega_k + (\alpha Z)^{-2} \right] \right] \right\}^{-1/2} \end{aligned}$$

It can be shown that at $r \rightarrow \infty$, $N(r) \rightarrow N_k$, where N_k is the normalization of functions f_k , g_k of continuous spectrum satisfying the condition (11). The energy of an electron formed due to a transition jkl is defined by the difference between energies of an atom with a hole at the j level and double-ionized atom at kl levels in the final state:

$$E_A(jkl, {}^{2S+1}L_J) = E_A^+(j) - E_A^{2+}(kl, {}^{2S+1}L_J) \quad (12)$$

To single out the above-mentioned correlation effects, the equation (12) can be presented as:

$$\begin{aligned} E_A(jkl, {}^{2S+1}L_J) &= \\ &= E(j) - E(k) - E(l) - \Delta(k, l; {}^{2S+1}L_J) \end{aligned} \quad (13)$$

where the item Δ takes into account the dynamic correlation effects (relaxation due to hole screening with electrons etc.) To take these effects into account, the set of procedures elaborated in the atomic theory [2,3] is used. For solid phase, the more precise form of equation (13) is [1]:

$$\begin{aligned} E_A^s(jkl, {}^{2S+1}L_J) &= \\ &= E_A(jkl, {}^{2S+1}L_J) + \Delta E^s + R_{rel} + e\Phi \end{aligned} \quad (14)$$

where ΔE^s is a correction for the binding energy change in the solid; R_{rel} , the same for out-of-atom relaxation; $e\Phi$ takes into account the work of exit. In real Auger spectra, a specific line shape characteristic for a given transition and for each element arises due to the line blurring caused by the Auger electron interaction with electrons of inner shells, outer bands, overlapping individual multiplet lines, multi-particle effects etc. In solids, the Auger spectra are broadened in the low-energy region due to non-elastic scattering of Auger electrons emitted by an atom when those move within the crystal [1].

Calculation results and conclusions

Now let us describe some calculated data for Auger electron energy in solids. As mentioned above, the exit probability of Auger electrons from an atom via different channels associated with ionization from a core level is defined by the matrix element (1). In addition, the proportionality coefficient in the equation coincides with the electron impact ionization cross-section σ_j of the level j . Of course, two aspects are to be considered when determining the exit probability of Auger electrons from an atom, namely, the radiative transition under neutralization of a hole at the level j and the possibility of a considerable change in the initial hole distribution at the core levels at the Auger decay via the radiative channel jkl associated as a rule with a considerable distinction in the non-radiative transition probabilities. For definiteness sake, let the ionization of L levels in a multi-electron atom be considered. The probability of the Auger electron emission from the atom via the channel L_3KL (taken as an example) is defined by the ionization cross-section of the level L_3 as well as by a certain effective cross-section depending on the ionization cross-sections of the levels L_p, L_2 . The Auger line intensity is defined by three atomic constants: $A_{jkl} = \sigma_j f_i a_{jkl}$, where a_{jkl} is the non-radiative transition probability; f_i is the Korster-Kronig coefficient; σ_j ,

the ionization cross-section defined by the matrix element (1) calculated for wave functions of bound state and continuum one.

In table 1 we present the data on Auger electron energy for some solids calculated using the gauge-invariant method of this work (column C), the semi-empirical method under Larkins' equivalent core approximation [2] (column A), the non-gauge-invariant QED PT [8] as well as experimental data (c.f.[2]). The calculation accuracy using method [2] is within about 2 eV as an average. Our approach provides more accurate results that is due to a considerable extent to more correct accounting for complex electron interaction. The improvement of our data in comparison with results [8] is connected with using the fully gauge-invariant scheme. To conclude, note that the use of the Auger electron spectroscopy in analysis of the surface chemical composition requires consideration of Auger spectra and the corresponding characteristics of the Auger transitions, interpretation of effects like the shape transformations of the valence Auger spectra due to appearance of new lines, position and intensity changes of individual lines caused by the redistribution in the electron state density of the valence band. The correct theoretical estimations of the spectral characteristics are of critical importance for their full understanding.

Table 1

Experimental data for Auger electron energy for solids and calculated values (A, semi-empirical method [2]; B, [8]; C — present paper)

Element	Auger line	Experiment	Theory: A	Theory: B	Theory: C
Na	$KL_{2,3}L_{2,3}^1D_2$	994,2	993,3	994,7	994,3
Si	$KL_{2,3}L_{2,3}^1D_2$	1616,4	1614,0	1615,9	1616,3
Ge	$L_3M_{4,5}M_{4,5}^1G_4$	1146,2	1147,2	1146,6	1146,2
Ag	$M_5N_{4,5}N_{4,5}^1G_4$	353,4	358,8	354,1	353,5

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