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Measurement and interpretation of the low-energy wing of Fe K$\beta_{1,3}$ characteristic X-ray line

P.S. Antsiferov[a], Yu.V. Ralchenko[b,*]

[a]Institute of Spectroscopy, Troitsk, Moscow Region 142092, Russia
[b]Faculty of Physics, Weizmann Institute of Science, Rehovot 76100, Israel

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Abstract

Special profile of Fe K$\beta_{1,3}$ characteristic line emitted by free atoms is measured and compared with the theoretical Hartree–Fock calculations. It is shown that the low-energy wing structure, which is not resolved in the emission in solid state, can be well described by the superposition of the profiles corresponding to the $^5D^4$, $^3P^4$ and $^3H^4$ parent terms of the 3d^6 shell. © 2001 Elsevier Science Ltd. All rights reserved.

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Since the beginning of the study of X-ray characteristic lines it is known that many of them have asymmetrical spectral profiles. Most often, this asymmetry is due to the structure of the line, which cannot be resolved by any high-resolution spectrometer because of large natural widths of individual components. One of the examples is the low-energy wing of the Kβ lines of the transition metals of Fe group. In the first attempt to ascertain the asymmetry of Cr Kβ line, it was found that this asymmetry correlates with the magnetic properties of different Cr compounds [1]. So, the exchange interaction between the hole state and the 3d shell electrons was proposed as the main mechanism of asymmetry under investigation. More detailed theoretical modeling [2] gave only a qualitative picture of the low-energy wings of the characteristic lines. The calculations for Ti, which has relatively simple outershell electron configuration 3d^{2}4s^2, gave a better description of the experimental profile of the Kβ line [3]. The situation is more or less clear with Cu, which has very simple outershell configuration 3d^{10}4s. The spectral profile of its Kβ line can be described by the 1s–3p hole transition with an 'admixture' of the 1s3d–3p3d hole transition [4,5]. The problem

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* Corresponding author. Fax: + 972-8-934-3491.
E-mail address: yuri.ralchenko@weizmann.ac.il (Y.V. Ralchenko).

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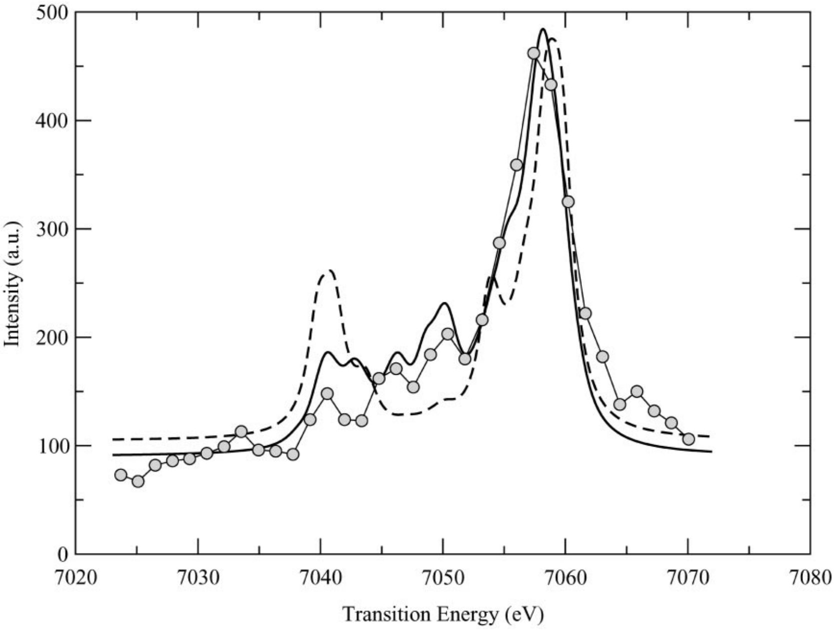

Fig. 1. The Fe K$\beta_{1,3}$ spectral profile: experiment — gray circles; the model profile corresponding to the $^5D^4$ term of the 3d^6 shell — dashed line; the best fit of the model profile including excited terms of 3d^6 shell — solid line.

of quantitative theoretical description of spectral profiles of X-ray characteristic lines is complicated by the interaction of atoms is crystalline lattice, since usually most of the characteristic lines are studied in the conditions of their radiation by the anode of X-ray tube. In present work, the spectrum of Fe K$\beta_{1,3}$ emitted by *free* atoms is investigated. As it was already shown [6], the free Fe atoms reveal the structure on the low-energy asymmetric wing of K$\beta_{1,3}$ which is not resolved in a solid state. In the present paper this spectrum is obtained in a wider spectral range and compared with the results of theoretical calculations.

The X-ray spectra of Fe K$\beta_{1,3}$ were measured using the method described previously [6,7]. The ionizing electrons are produced by an electron gun that can work in two regimes with different currents. In the X-ray tube mode, it produces an electron beam with the current of 0.5 mA and the working voltage up to 15 kV. In the regime of the study of Fe vapor, the gun current is increased up to 20 mA, the beam being able to melt the anode and evaporate it. The pulsed mode with the pulsetime 0.1–1 s allows us to study a vapor of practically any metal without the use of high-temperature furnaces. The spectrometer unit contains the X-ray monochromator with the bend quartz crystal (2d = 2.37 Å, R = 450 mm), the entrance slit (0.1×0.5 mm^2) on the Rowland circle and the proportional gas X-ray counter. The metallic vapor in front of the entrance slit is ionized by the same electron beam. The scanning of the spectrum is produced by displacement of the unit with bend crystal and X-ray counter. The estimated resolution of the spectrometer is about 30% of the visible linewidth. The experimental profile of the Fe K$\beta_{1,3}$ lines of free atoms is presented in Fig. 1 (gray circles).

The calculation of the transition wavelengths and radiative probabilities for transitions in Fe II was carried out with the Hartree–Fock-relativistic (HFR) code of Cowan [8] with account of configuration interaction and intermediate coupling. The following configurations were included in calculation: even configurations $\underline{1s}3d^64s^2, \underline{1s}3d^74s, \underline{1s}3d^8$, $\underline{1s}3d^64s4d, \underline{1s}3d^74d$ and the corresponding odd configurations with the filled $1s^2$ shell and a hole in the 3p shell after the 1s–3p Kβ transition ($\underline{3p}3d^64s^2$, etc). The underlined shell ($\underline{1s}$) indicates the location of the hole, and other filled shells, such as $2s^2$, etc., are not explicitly indicated. The total number of levels in the present calculation was over 12 000. The scaling factors of 0.80 were used to correct the ab initio Slater parameters. This number, being close to the value of 0.85 implemented in the study of the Fe I spectra [9], was found to provide slightly better agreement with the experimental spectrum.

The presence of a hole in the 1s shell results in significant changes in the distribution of energy levels comparing to a neutral atom. While the configuration $3d^64s^2$ is the lowest one for the Fe I atom, the lowest configuration of Fe II with a hole in the 1s shell is $\underline{1s}3d^8$ followed by $\underline{1s}3d^74s$ and $\underline{1s}3d^64s^2$. The present calculations show that the difference in the average configuration energy between these three configurations is $E_{av}(\underline{1s}3d^74s) - E_{av}(\underline{1s}3d^8) \approx 1\,\text{eV}$ and $E_{av}(\underline{1s}3d^64s^2) - E_{av}(\underline{1s}3d^74s) \approx 5$ eV. It should also be mentioned that all these configurations have quite a large energy spread reaching, e.g., 10 eV for $\underline{1s}3d^64s^2$.

The lowest terms of the upper $\underline{1s}3d^64s^2$ configuration are $(^5D^4)^{6,4}D$, $(^3H^4)^{4,2}H$, $(^3P^4)^{4,2}P$, $(^3F^4)^{4,2}F$, etc., where the parent term of $3d^6$ is given in parentheses with the second superscript being the seniority quantum number. It was assumed in our modeling that the population distribution within each of the $\underline{1s}3d^64s^2$ terms corresponding to the same *parent* term of $3d^6$ is proportional to the statistical weights of the levels. The present ab initio calculation of the Kβ transition energies gives values that are higher than the experimental ones by about 0.15%. Although this accuracy seems to be acceptable for the HFR code, we ought nevertheless to shift all theoretical lines by 11 eV (the transition energy is ~ 7060 eV) in order to produce the best fit of the experimental spectrum. Then, each of individual lines was convoluted with the FWHM = 2.5 eV Lorentzian profile simulating the instrumental broadening. Since the ground state term of the neutral Fe I is $^5D^4$ and assuming that the electron impact ionization of the inner 1s electron does not cause the rearrangement of the outer shells, one would have to use only the $(^5D^4)^{6,4}D$ terms of the configuration $\underline{1s}3d^64s^2$ to model the experimental spectrum. Such a model profile, shown by the dashed line in Fig. 1, correctly describes the doublet splitting of the transition but does not reproduce the profile features near 7045 and 7050 eV. Therefore, the other terms of the upper configuration are to be added in order to generate a proper fit of the measured spectrum. The number of terms included into the fitting procedures was variable, and the addition of configuration other than $\underline{1s}3d^64s^2$ does not noticeably improve the fit. The best fit (solid line in Fig. 1) was obtained with the following linear combination of term populations $N(^{2S+1}L)$:

$$\mathit{Profile} = \mathit{const} + N(^5D^4) + 2.07N(^3H^4) + 4.44N(^3P^4), \tag{1}$$

where $^5D^4$, $^3H^4$ and $^3P^4$ are the lowest terms of the $3d^6$ shell; a constant reflecting the background spectrum was also added. One can see from Fig. 1 that the spectral structures in the range 7040–7060 eV are described reasonably well. The account of additional terms of the initial configuration having higher energies gives rise to negative weights with no visible improvement in fit quality, and thus they were discarded. It should be noted that the fitting weights in (1) increase with the term energy. This indicates that both $^3H^4$ and $^3P^4$ terms seem to be overpopulated compared to the lowest term $^5D^4$. Obviously, it cannot be caused by a shake-up process that does not change the quantum numbers. On the other hand, the radiative Auger effect would result in transitions with the energy differing by the electron temperature and density in vapor are so small ($T_e \ll 1$ eV and $N_e \sim 10^{14}$ cm^{-3}) that one would not expect any substantial excitation into $^3H^4$ and $^3P^4$ from the ground term. The reason for this overpopulation is currently under study and the results will be published elsewhere.

In conclusion, we have shown here that the low-energy wing structure of the free-atom Fe $K\beta_{1,3}$ characteristic line can be attributed to the intra-configuration excitation of the $3d^6$ shell into the $^3H^4$ and $^3P^4$ terms in the process of the creation of inner-shell vacation.

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