Kinetic analysis of sample degradation progress curves

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Rare-gas solids are the model systems in physics and chemistry of solids, and a lot of information about their electronic excitations has been documented in several books and reviews (see e.g. Ref. 1 and references therein). The subthreshold inelastic radiation-induced atomic processes in rare-gas solids such as defect formation and desorption under excitation by photons and electrons with a kinetic energies below the threshold of knock-on of atoms from the lattice sites were studied recently [1]. However, to our knowledge, the kinetic analysis of the dose curves of electronic excitation induced accumulation of crystal lattice imperfections was not done up to now.

In the present paper we propose the simple kinetic model for radiation-induced defect accumulation processes, which may be used for certification and comparison of rare-gas samples. The experiments were carried out at the SUPERLUMI-station at HASYLAB, DESY, Hamburg. The selective photon excitation was performed with spectral resolution $\Delta\lambda$=0.2 nm. The VUV-luminescence analysis was performed both with low-resolution, $\Delta\lambda$=2 nm, Pouey high-flux monochromator equipped with a multisphere plate detector and with high-resolution, $\Delta\lambda$=0.1 nm, secondary 1 m near-normal incidence monochromator equipped with a position-sensitive detector.

Figure 1 shows examples of evolution of luminescence spectra of solid Xe and Ne under irradiation by photons with energies $E<E_g$. An increase in the intensity of the defect component during irradiation reflects the accumulation of stable long-lived defects in the lattice as a result of exciton creation and self-trapping. The process of defect accumulation may be written as consecutive process $E+T \leftrightarrow S \rightarrow D$ [2], where *E* is the mobile excitation (e.g. free exciton), which is trapped at trapping center *T* (e.g. lattice imperfection) and, with a rate constant f_S, forms an excited metastable trapped center *S* (e.g. A-STE, or M-STE), which can be considered as metastable short-lived lattice defect.

Radiative decay of the short-lived *S*-center either with a rate constant f_{-S} returns the lattice into the initial state without permanent defect, or forms the permanent defect *D* (Frenkel pair) in the reaction $S \rightarrow D$ with a rate constant f_D. We may represent the number of mobile excitations per irradiated volume, c_E, as: $c_E = \Omega \cdot t$, where parameter Ω is a function of photon irradiation efficiency, life-time of mobile excitation, quantum yield of luminescence and luminescence detection efficiency by secondary monochromator, detector and electronics. This parameter may be assumed as constant for the dose curves, which are measured under identical conditions. The initial number of trapping centers per irradiated volume, c_T^0, is a sum of current values of c_T and c_S. The time dependence of luminescence intensity of 'defect' subband under steady-state conditions may be expressed in form:

$$I(t) = I_0 + \frac{K \cdot t}{L + t}, \quad (1)$$

where $I_0 = I(0)$ is the initial intensity of 'defect' luminescence due to $c_T^0 \neq 0$; $K = f_D c_T^0$ is the saturation value of $(I(t) - I_0)$ at $t \rightarrow \infty$; $L = (f_{-S} + f_D)/(f_S \cdot \Omega)$ is a characteristic constant of a sample – under identical excitation and detection conditions the sample with less pronounced processes of defect formation will have a bigger value of L. Fig. 1(c,d) show the examples of fitting by Eq. (1) the dose curves of 'defect'-components "1" of solid Xe and Ne.

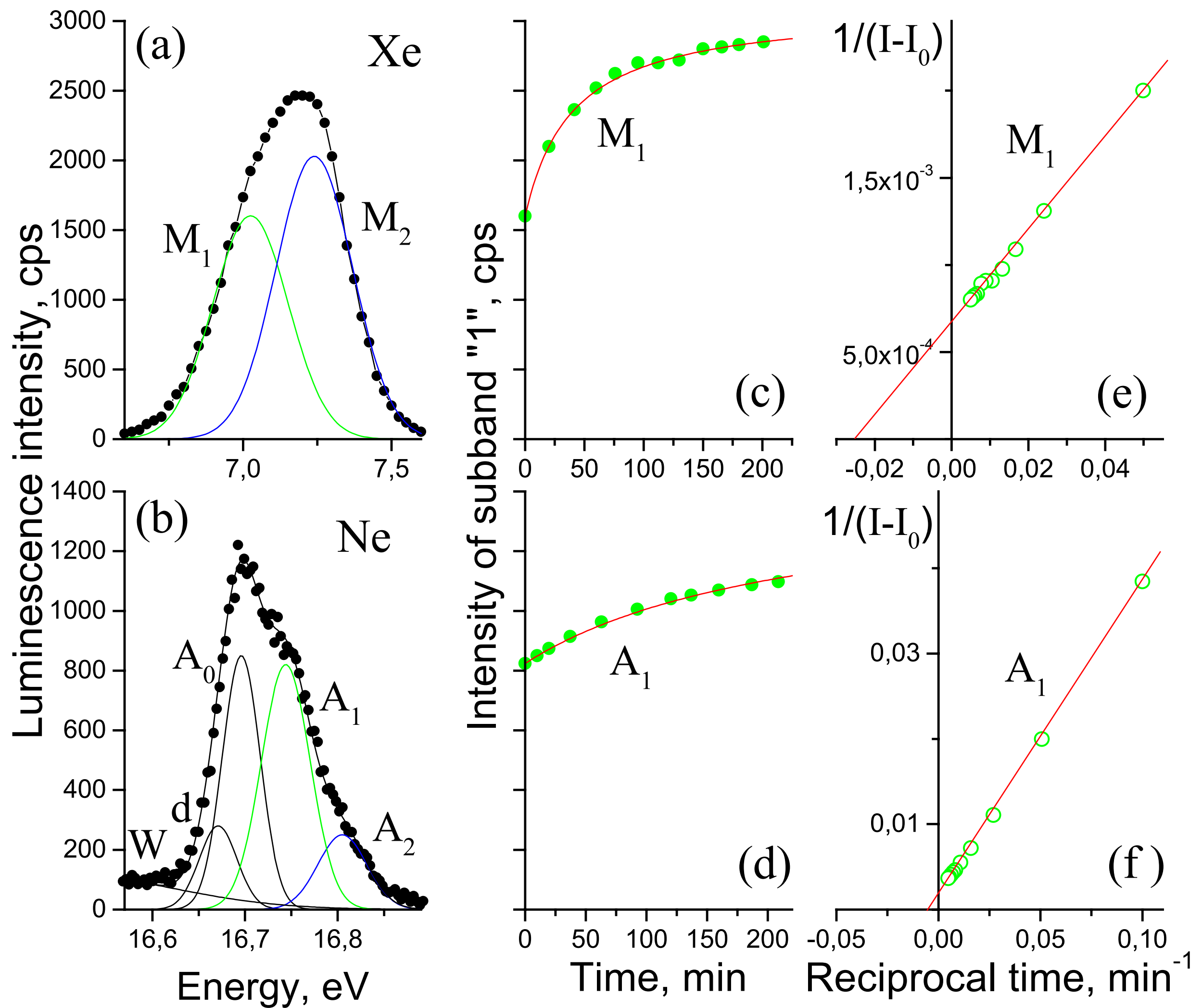

Figure 1: Internal structure (a,b), dose dependences (c,d) and fitting of data in double reciprocal plots (e,f) of luminescence bands of solid Xe (a,c,e) and Ne (b,d,f) at T=5 K under photoexcitation with energies $h\nu$=9.15 eV (Xe) and $h\nu$=20 eV (Ne).

Linear transformation of Eq. (1) in the form $\left(I(t)-I_0\right)^{-1}=K^{-1}+L\cdot\left(K\cdot t\right)^{-1}$ allows us to determine the values of constants K and L from interceptions with axis of double reciprocal plot of the straight line of data linear fit (Fig. 1(e,f)). In the particular case of Fig. 1 the values were $K_{\mathrm{Xe}}=1500$ cps, $K_{\mathrm{Ne}}=620$ cps, $L_{\mathrm{Xe}}=40$ min, $L_{\mathrm{Ne}}=230$ min, which is in line with general increase of defect formation efficiency in the sequence: Ne, Ar, Kr, Xe. Analytical applications of this method enable a comparison of different rare-gas crystals with standard one and estimation the radiation doses from initial part of the dose curves, and provide a way of qualitative and quantitative analysis and certification of rare-gas crystals, which is indispensable at any attempt of comparison of data from different samples.

References

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