Photoelectron spectroscopy as a probe for studying phase-transition kinetics

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Photoelectron spectroscopy (PES) can be profitably employed for studying three-dimensional phase-transition kinetics as long as the problem of finite escape depth and the presence of the surface is correctly taken into account. A general solution of this problem is presented for transformations following the Johnson-Mehl-Avrami-Kolmogorov kinetics. The cases of simultaneous and constant nucleation rates are discussed. We found that the simple relationship between the PES signal $I(t)$ and the untransformed phase $X(t)$: $I(t) = I(0)X(t)^{1/2}$ is an excellent approximation for the simultaneous nucleation and turns out to be quite good for the constant nucleation case. [S0163-1829(97)50418-8]

Phase transitions represent a fundamental topic in materials science.[1] A large variety of transformations in solids have been numbered which covers the polymorphism of both one-component systems and pure substances, as well as the much more complex transitions (driven by changes of temperature and composition) occurring in nonstoichiometric compounds. Phase transformations involving a metastable phase, stable to fluctuations, are usually described by nucleation and growth processes. The kinetics of these transformations are widely studied through the phenomenological model referred to as Johnson-Mehl-Avrami-Kolmogorov (JMAK).[2–4] On the experimental side, several techniques have been employed for measuring phase-transition kinetics which, depending upon the kind of transformation, include diffraction and optical methods, electrical and magnetic measurements, thermal methods, and so on.[1] The time dependence of the measured transformed volume, $V(t)$, is commonly presented in the form of linear Avrami's plots, namely, $\ln[-\ln(1-V(t))]$ vs t, which implies a stretched exponential function for $V(t)$: $V(t) = 1 - X(t) = 1 - \exp(-kt^n)$, being k and n constants.[5,6] Accordingly, the k and n parameters are derived from experimental data and their temperature dependence is commonly analyzed on the ground of Arrhenius plots. However, it is worth noting that in the framework of JMAK theory such a function is only obtained for either continuous or simultaneous nucleations, provided the growth law is a time power.

Although the photoelectron spectroscopy has been used for investigating some aspects of transformations in solids,[7,8] it has never been exploited for studying the kinetics, mainly for three reasons: (i) the data acquisition time must be much shorter than the characteristic time scale of the transition; (ii) the finite electron escape depth affects the actual kinetic curve, in fact reducing the bulk contribution through the attenuation factor; (iii) the presence of the surface strongly modifies the bulk kinetics within a distance from the surface, of the order of the nucleus diameter.

The third generation synchrotron radiation sources meet the requirements of short acquisition time [point (i)], and open up new horizons in the study of nucleation and growth kinetics in real time.[9] In order to promote photoemission to a suitable technique for measuring kinetics, it is compulsory to face the escape depth problem, i.e., to extract the real kinetics from the measured one. Once this task is achieved, a kinetic-photoemission experiment would provide quantitative information on the electronic structure of the transforming solid as well as on the kinetic behavior of the phase transition, determining the k and n kinetic parameters. Photoelectron spectroscopy (PES) would be a rather powerful technique for getting insight into phase transformations in solids.

Let us consider the polymorphic phase transformation of a one-component solid, occurring by nucleation and growth mechanisms. The assumption is here made that it is possible to distinguish from the measured photoemission spectra the contribution of the untransformed and transformed phases.[8] At running time t the photoemission signal of the untransformed phase is[10]

$$I(t) = \frac{I(0)}{\lambda} \int_0^\infty Z(x,t)e^{-x/\lambda}dx, \qquad (1)$$

where λ is the effective escape depth, x is the distance from the surface, and $Z(x,t)$ is the probability the points belonging to the plane parallel to the surface, at x, are not transformed at time t. Clearly $Z(x,0) = 1$.

In order to develop the $Z(x,t)$ expression, the boundary layer effects due to the presence of the surface must be taken into account. Weinberg and Kapral's work[11] is quite in keeping to this end but, whereas they employed a lattice approach, here the system is considered as a continuum. Moreover, as in Ref. 11, nuclei are cubic and the nucleation occurs at random in the volume. The $Z(x,t)$ kinetics is computed according to

$$Z(x,t) = \Theta[b(t)-x]\exp\left(\int_0^{\bar{t}}\ln W(x,t,z)dz + \int_{\bar{t}}^t \ln A(t,z)dz\right)$$
$$+ \Theta[x-b(t)]\exp\left(\int_0^t \ln A(t,z)dz\right), \qquad (2)$$

where $\Theta[y]$ is the Heaviside function, $W(x,t,z) = e^{-4(dN/dz)b(t-z)^2[b(t-z)+x]}$, $A(t,z) = e^{-8(dN/dz)b(t-z)^3}$, $2b(t-z)$ being the edge of the cluster nucleated at time z,

and dN/dz is the nucleation rate. The $\bar{t}(x)$ function is defined through the equation $x = b(t-\bar{t})$. Inserting the W and A functions, Eq. (2) becomes

$$Z(x,t) = \Theta[b(t)-x]\exp\left[-4\int_0^{t-b^{-1}(x)}\frac{dN}{dz}b(t-z)^2[b(t-z)+x]dz - 8\int_{t-b^{-1}(x)}^t\frac{dN}{dz}b(t-z)^3dz\right]$$

$$+\Theta[x-b(t)]\exp\left[-8\int_0^t\frac{dN}{dz}b(t-z)^3dz\right]. \tag{3}$$

The simplest case that can be studied is the simultaneous nucleation rate, that is $dN/dz = N_0\delta(z)$, where δ is the Dirac delta function and N_0 the number of nuclei per unit volume. Substituting the last expression into Eq. (3), Eq. (1) becomes

$$I(t) = I(0)\left[X(t)^{1/2}\frac{1-X(t)^{1/2}e^{-b(t)/\lambda}}{\left(1+\frac{\lambda S_e(t)}{6}\right)}+X(t)e^{-b(t)/\lambda}\right], \tag{4}$$

where $X(t) = e^{-8N_0b(t)^3}$ is the volume fraction of the untransformed phase, $S_e(t) = 24N_0b(t)^2$ is the "extended surface" of the nuclei.[3,12,13] As it is commonly in use in Avrami's theory, the term extended refers to quantities computed regardless of the effect of impingement among nuclei. When the condition $[\lambda S_e(t)/6] \ll 1$ is fulfilled, the kinetics Eq. (4) leads to the following striking and extremely simple form:

$$I(t) = I(0)X(t)^{1/2}. \tag{5}$$

The photoemission signal is related to the square root of the *bulk* untransformed fraction, and any coupling between the microscopic growth law $[b(t)]$ and the escape depth (λ) disappears. In fact, the previous inequality is satisfied, practically, for the whole kinetics. Indeed, at 99% of the transformation ($X = e^{-V_e} \cong 0.01$) the extended volume V_e, is $V_e = 4.61$, and the following inequality can be easily obtained: $S_e(t) \leq 17N_0^{1/3}$. Accordingly, a sufficient condition to have $(\lambda S_e(t)/6) \ll 1$ up to 99% transformed volume, is $\lambda \ll (1/2.8N_0^{1/3}) = \bar{d}/2.8$, where $\bar{d}$ is the average distance between grains. The last inequality could be verified since λ is of the order of a few angstroms while $\bar{d}$ easily reaches hundreds of angstroms.

The second interesting case is the constant nucleation rate which occurs in phase transformations once the steady-state condition is reached. The assumption is made of a constant growth rate of the nucleus edge, $b(t-z) = v(t-z)$, where v is the rate of nucleus growth. By specifying in Eq. (3) the range of integration $[t-b^{-1}(x) = t-(x/v)]$ and computing the integrals, the photoemission kinetics Eq. (1) becomes

$$I(t) = \frac{vt}{\lambda}I(0)X(t)^{1/2}\int_0^1 X(t)^{-\eta^4/6}X(t)^{2\eta/3}e^{-vt\eta/\lambda}d\eta$$

$$+I(0)X(t)e^{-vt/\lambda}, \tag{6}$$

where $X(t) = e^{-2\nu v^3 t^4}$ is the fraction of the untransformed phase at time t, and ν is the nucleation rate. It can be shown that the approximation $X^{-\eta^4/6} \approx 1$ can be reasonably employed. As a matter of fact, for $X > 0.5$, i.e., $0 < V < 0.5$, such an approximation implies an error lower than 2% whereas for $0.5 < V < 0.95$ the error ranges 2–9 %. In this limit the photoemission kinetics reads

$$I(t) = I(0)\left[X(t)^{1/2}\frac{1-X(t)^{2/3}e^{-vt/\lambda}}{\left(1+\frac{\lambda S_e(t)}{6}\right)}+X(t)e^{-vt/\lambda}\right], \tag{7}$$

where $S_e(t) = 8\nu v^2 t^3$. Even in this case $[\lambda S_e(t)/6] \ll 1$ and the resulting expression, $I(t) = I(0) \times [X(t)^{1/2}+e^{-vt/\lambda}(X(t)-X(t)^{7/6})]$, takes, within the same order of approximation which leads to Eq. (7), the same form as Eq. (5).

The modeling shows that, for both studied nucleation rates, the effect of the boundary surface strongly determines the expression of the photoemission current. The very simple form of Eq. (5) is an excellent approximation for the actual kinetics within the assumption of the model. Moreover, once the phase to be followed is established, say α, so as to determine the fraction of untransformed volume, X_α, the knowledge of the "direction" of the phase transformation is
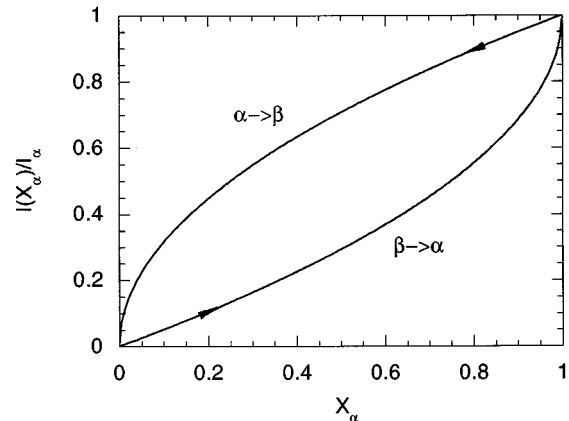

FIG. 1. Behavior of the α photocurrent as a function of the bulk fraction of the α phase. According to whether X_α is the untransformed ($\alpha \rightarrow \beta$) or transformed ($\beta \rightarrow \alpha$) fraction, the photocurrent assumes different values under the same X_α.

required. As a matter of fact, in going from α to β the PES signal is $I_\alpha(t) = I_\alpha X_\alpha(t)^{1/2}$, whereas from β to α phases it is $I_\alpha(t) = I_\alpha[1 - \sqrt{1 - X_\alpha(t)}]$ (Fig. 1).

In passing it is worth citing the possibility to determine, experimentally, whether or not the aforementioned condition $\{[\lambda S_e(t)/6] \ll 1\}$ is fulfilled. Thanks to the tunability of the photon energy in synchrotron radiation sources, several ki-netics can be worked out at different λ values and the break-down of the inequality ought to manifest itself by a nonover-lapping of the kinetics.

In conclusion we demonstrate that PES can be exploited to investigate phase-transition kinetics. Notably, we found out that, within a very good approximation, a simple relation links the actual three-dimensional kinetics to the PES signal.

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