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^{63}Ni diffusion in C_{60} fullerite

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The possibility to obtain in principle metal-fullerides using diffusion methods has been established using radioactive isotopes (^{63}Ni). The thermally activated diffusion (T = 300°C) in fullerite crystal has been assumed to occur according to the interstitial mechanism via successive filling of octa- and tetrahedral pores. The basic quantitative characteristics of diffusion in a fullerite crystal: diffusion coefficient $D \sim 10^{-12}$ cm^2/s, β-radiation absorptance in fullerite $\mu = 3.94 \cdot 10^4$ cm^{-1} and dynamics of its diffusion saturation with the metal atoms have been determined.

С помощью радиоактивных изотопов (^{63}Ni) установлена принципиальная возможность получения металлофуллеридов диффузионными методами. Предположено, что в кристалле фуллерита термически-активированная (T = 300°C) диффузия происходит по междоузельному механизму при последовательном заполнении окта- и тетраэдрических пор. Получены основные количественные характеристики диффузии в фуллеритовом кристалле — коэффициент диффузии $D \sim 10^{-12}$ см^2/с, коэффициент $\mu = 3.94 \cdot 10^4$ см$^{-1}$ поглощения β-излучения фуллеритом и динамика его диффузионного насыщения атомами металла.

The manufacturing of endofullerenes directly during the fullerene formation limits strongly the possibility of further influence on their properties. One of the methods to influence on the fullerene electronic properties is the forced implantation of non-carbon atom into the shell of C_{60} molecule. This requires a partial destruction of thin (about 1 Å) molecular shell and can be carried out by ionic bombardment, for example, in the glow discharge plasma [1]. On the other hand, when being deposited onto a substrate, C_{60} molecules form a fcc crystal lattice. It is obvious that in such a crystal, the same thermodynamical processes occur that are inherent in a condensed solid. In particular, due to diffusion, when all interstices becomes filled, there a new matter of Me_3C_{60} type may appear, possessing a quite different electronic structure. Therefore, the control of electrophysical parameters of fullerides by changing their electronic structure with non-carbon atoms embedded into fulleride crystal is of particular importance. In this work, the possibility of metal diffusion in the fullerite film lattice has been studied using radioactive isotopes.

A variation of absorption method based on the control of radioactive radiation intensity passing through the investigated material with an absorptance μ was used in the studies. The sample formed as a stainless steel substrate was electrolytically coated by a layer of ^{63}Ni isotope until reaching the activity suitable for further diffusion experiments. The surface radioactivity was measured in a "Beta" analyzer using cooled PMT and special cuvette filled with scintillation liquid. The sample surface to be examined was placed at some distance above the surface of scintillation liquid. The initial radioactivity appeared to be equal 660 decays/min. Then the radioactive layer was covered by a d_f = 0.2 μm thick fullerite

film deposited in vacuum (10^{-5} Torr) by sublimation method (T = 500°C). Our previous X-ray diffraction analysis [1] showed that films obtained in the same conditions are crystalline. The surface radioactivity of the sample shielded by fullerite film decreased to 300 decays/min.

Thereafter, the sample was subjected to a series of homogenizing annealing procedures in vacuum under monitoring of surface radioactivity up to restoration of its initial value. The annealing temperature (T = 300°C) was chosen taking into account that it should not be sufficient for possible fullerite sublimation but sufficient for realization of diffusion processes. The annealing temperature was to within ±10°C. The fullerite film integrity preservation in spite of its sublimation during annealing procedures, although it was almost improbable, could be evidenced by the absence of fullerite traces on the polished surface of the glass ceramics plate, which was a technological element in the experiment and placed in the close proximity to the film being annealed.

Figure presents the determination results of the sample surface radioactivity (dots) as a function of homogenizing annealing time. The data obtained show that during 8 hours, Ni atoms diffused through the fullerite lattice and completely filled the fullerite film. A simple estimation gives the diffusion coefficient: $D \sim d_f^2/t = 1.4 \cdot 10^{-12}$ cm^2/s. The absorptance μ of the fullerite film can be calculated using a well known dependence

$$I_x = I_0 \exp(-\mu x) \qquad (1)$$

characterizing the absorption of radiation by a shielding layer of thickness x with the absorptance μ. This allows calculate the absorptance of β-radiation from ^{63}Ni radioactive atoms in C_{60} fullerite: $\mu = 3.94 \cdot 10^4$ cm^{-1}. The fullerite fcc lattice constant is a = 14.2 Å, interatomic spacing on the cube diagonal is 10.04 Å. Taking into account a rather small size of metal atoms ($r_{Ni} \sim 1.62$ Å) with respect to characteristic distance in the fullerite unit cell and also such a high value of the diffusion coefficient, it is possible to assume that atom migration occurs most likely according to interstitial mechanism through octa- and tetrahedral interstices of fullerite crystal. The metal atoms occupy first of all the octahedral interstices as they are bigger than tetrahedral ones. Even

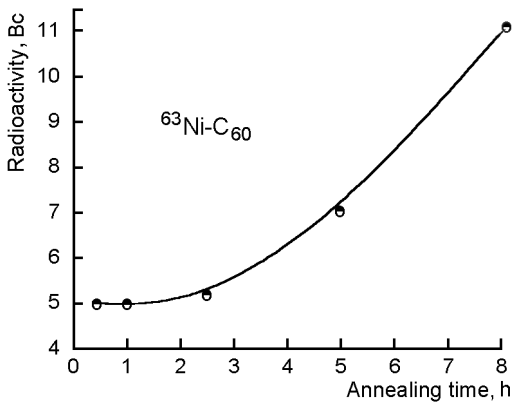

Fig. Dynamics of ^{63}Ni atoms penetration through the C_{60} fullerite film (T = 300°C).

higher probability of interstitial diffusion exists for metal ions having in the case of Ni radius of ~0.69 Å. This value is much smaller than even intermolecular distances in the fullerite unit cell.

The analysis shows that the obtained surface radioactivity change can be best described by a semiempirical equation which takes into account diffusion of labelled atoms through the film of the thickness d_f with the absorptance μ from the source having the intensity I_0

$$I(t) = I_0 \left[\exp(-\mu d_f) + \right. \qquad (2)$$
$$\left. + 2\pi \cdot \operatorname{erfc}\left(\mu^2 (d_f^2 - \pi D t)\right) \cdot \operatorname{erfc}\left(\frac{d_f - \sqrt{\pi D t}}{2\sqrt{\pi D t}}\right) \right].$$

It is seen from the above equation that at the initial time moment, i.e. $t \to 0$, the second item is zeroed because of the second factor ($\operatorname{erfc}(\infty) = 0$), and we return to the equation (1). At $t > 0$, the second component gives its contribution and radioactivity on the sample surface increases due to isotope diffusion through the film of the thickness d_f. As time goes by ($t \to \infty$), the metal atoms penetrate into fullerite film with the diffusion coefficient D and film becomes saturated by metal atoms resulting in the increase of intensity $I(t)$ on the film surface.

It should be noted that equation (2) is applicable for specific experiment conditions, although it does not fully take into account the exhaustion of the diffusion source. Calculations according to this equation are presented in Figure as a solid line. A good correlation is seen between experimental data and the calculated curve ob-

tained for $D = 2.0 \cdot 10^{-12}$ cm^2/s. This may be connected with the difference between the preexponential factor D_0 and typical values in the known equation for thermal diffusion $D = D_0 \exp(-Q/kT)$. This factor is known to be in proportion with the square of the elementary jump distance of a point defect, i.e. approximately with the square of the average interatomic or intermolecular distance: $D_0 \approx \lambda^2/2\tau_0$. Considering that characteristic period of the defect oscillation is $\tau_0 \sim 10^{-12}$ s and taking λ as an average distance between octa- and tetrahedral interstices in the fullerite crystal, which is approximately 1.41 nm, it is possible to estimate the energy Q of diffusion activation. Taking into account all aforesaid, the calculated value corresponds to the activation energy of the migrating interstitial type point defects and supports the hypothesis about the diffusion of metal atoms along interstices of fullerite crystal.

References

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Дифузія атомів ^{63}Ni у фулериті на основі C_{60}

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З використанням радіоактивних ізотопів (^{63}Ni) встановлено принципову можливість отримання металофулеридів дифузійними методами. Припущено, що у кристалі фулериту термічно-активована дифузія (T = 300°C) відбувається за міжвузельним механізмом при послідовному заповненні окта- та тетраедричних порожнин. Отримано основні кількісні характеристики дифузії у фулеритовому кристалі — коефіцієнт дифузії $D \sim 10^{-12}$ см^2/с, коефіцієнт поглинання β-випромінювання фулеритом $\mu = 3.94 \cdot 10^4$ см$^{-1}$ та динаміка його дифузійного насичення атомами металу.