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RAPID DIFFUSION OF BISMUTH AND POLONIUM IN LEAD TO THE SURFACE STIMULATED BY PLASTIC DEFORMATION

Summary. Measurements and the quantitative analysis of the kinetics of the phenomenon of increasing radioactivity of lead after the scraping of the surface are presented. The growth of radioactivity concerns the alpha radioactivity of polonium and in a lower degree also the beta radioactivity of bismuth. When surface is scraped, the layer of the material near the surface is plastically deformed. Generated defects facilitate the diffusion of polonium and bismuth radioisotopes to the surface where the thermodynamic potential is lower than inside the material.

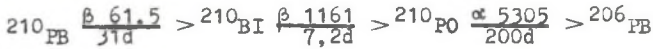
Introduction

After preliminary information [1-3] more systematic investigations of the effect of changes in the surface radioactivity of lead were presented in paper [4]. The conclusions of this paper are as follows:

- *) After the scraping of the lead surface, the measured alpha radioactivity A_0 is lower than before and versus time it increases to a steady state value $A_0 + \Delta A$. The increment ΔA is comparable to A_0 .
- *) The increase of radioactivity can be roughly approximated by the exponential relation with characteristic time of a several up to 30 days.
- *) Value of A_0 is characteristic for the given material, but both ΔA and the build-up time are different.
- *) When the sample was stored in air, the increase of radioactivity was very slow. The oxidation of the surface is responsible for this effect. Also when the sample was stored at a lower temperature, the increase of radioactivity was very slow.
- *) According to the postulated qualitative hypothesis, the radioactivity A_0 results from the equilibrium density of the radioisotope ^{210}Po - the product of the decay of ^{210}Pb i.e. a natural contamination of lead. The increase of radioactivity is caused by the fact, that the free energy of polonium atoms is lower at the surface of the crystal. Therefore, the polonium atoms accumulate on the surface in the diffusion process, and

consequently the density of the polonium atoms is lower inside the material to a depth determined by the state of kinetic equilibrium.

The natural contamination of lead, i.e. the radionuclide ^{210}Pb , decays in the sequence



The kind and energy of decay are given above the arrow, the average life time below. If N_0 denotes the density of polonium atoms in the steady state, τ is its mean life time and R the range of polonium alpha particles in lead ($10,6 \mu\text{m}$), then the alpha radioactivity of a unit of the surface in the steady state is equal to

$$A_0 = \frac{N_0 \cdot R}{4 \cdot \tau}, \quad \text{oraz} \quad \frac{N_0}{\tau} = \frac{N_1}{\tau_1} = \text{const} \quad (1)$$

Where τ_1 and N_1 denote the mean life times and densities of the other radionuclides in the decay series.

According to the quoted hypothesis, the profile of the density $N(x, t)$ of polonium versus the depth x measured from the surface into material, at a given moment of time is shown in Fig. 1. Typical values of A_0 measured for lead of a new production are equal to about $0,22 \text{ cpm/cm}^2$. This corresponds to the density of polonium atoms about $2,4 \cdot 10^8 \text{ cm}^{-3}$ or to the density of ^{210}Pb $1,3 \cdot 10^{-10} \text{ cm}^{-3}$. Basing on experimental values of ΔA it can be calculated, that one additional atom of ^{210}Po on the surface corresponds to $10^8 - 10^9$ atoms of lead. New experimental results and a quantitative interpretation explaining the mechanism and kinetics of the phenomenon are presented in this paper.

Experimental

Lead of a new production, with contaminations of heavy elements less than $10^{-3}\%$ was used for measurements. The samples had the shape of disks with a surface area of 200 cm^2 . Alpha radioactivity was measured by means of scintillation techniques. A photomultiplier with a diameter a little larger than the diameter of the sample, covered directly with activated zinc sulphide was situated 3 mm above the sample surface.

The sample with a photomultiplier was placed in an air tight chamber rinsed by inert gas. The heating of the sample could be controlled up to 50°C . In another vacuum chamber the sample could be stored at a temperature of up to 100°C . In such a case the sample was placed in the measuring chamber only for the time of measuring.

The counts were recorded every 100 minutes. The background of the measuring stand amounted to about 5,2 cpm. The results of measurements are presented in figures with their Poisson errors.

The individual measurements of beta radioactivity were made by means of the technique described in [4]. The surface of the sample was scraped by machining. Etching was accomplished by means of nitric acid.

Results and their analysis

In Fig. 2a there are presented measurements of the increasing alpha radioactivity after the scraping of the surface, stored first 12 days at room temperature and next at 100°C. An enlarged picture of the first part of the measurements is shown in Fig. 2b. At room temperature, as can be seen, the process nearly reached a steady state after 10 days. But the increase of the temperature activates the process, and new steady state on a much higher level of radioactivity was reached after about 100 days.

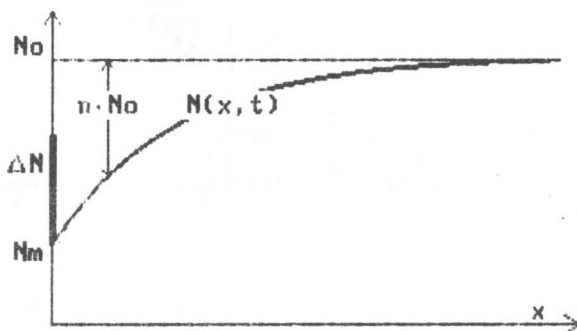


Fig. 1. Hypothetical profile of the volumetric density $N(x, t)$ of polonium at a given moment of time t versus the coordinate x measured from the surface towards the interior of the material. The perpendicular part of the diagram shows the surface density ΔN of additional atoms of polonium on the surface

Rys. 1. Hipotetyczny profil (wykresu) gęstości objętościowej $N(x, t)$ polonu w danej chwili t jako funkcja współrzędnej x mierzonej od powierzchni w kierunku wnętrza materiału. Część wykresu przedstawia gęstość powierzchniową ΔN dodatkowych atomów polonu na powierzchni

These results confirm the diffusive character of the transport of polonium. If this hypothesis holds true, the ratio of the densities of polonium N_m and N_0 (see Fig. 1) is of the order of the Boltzmann factor $\exp(-\Delta G/kT)$, where ΔG is the difference of the work function of the polonium atoms inside the material and on the surface. The fact that in spite of increasing temperature, the effect does not decrease but even stron-

gly increases, demonstrates that the value of ΔG is sufficiently large for accepting the value of N_m to be equal to zero in room temperature.

Another sample of the same kind of lead was conducted to its steady state at a higher temperature, similarly as in Fig. 2, and then the temperature was lowered to room temperature and measurements were started. The results are shown in Fig. 3. The decrease of radioactivity can be precisely approximated by means of the exponential relation with the time constant equal to the mean life time of ^{210}Po . These results confirm, that the excess of polonium atoms is bounded firmly with the surface and only by radioactive decay the system reverts to a steady state.

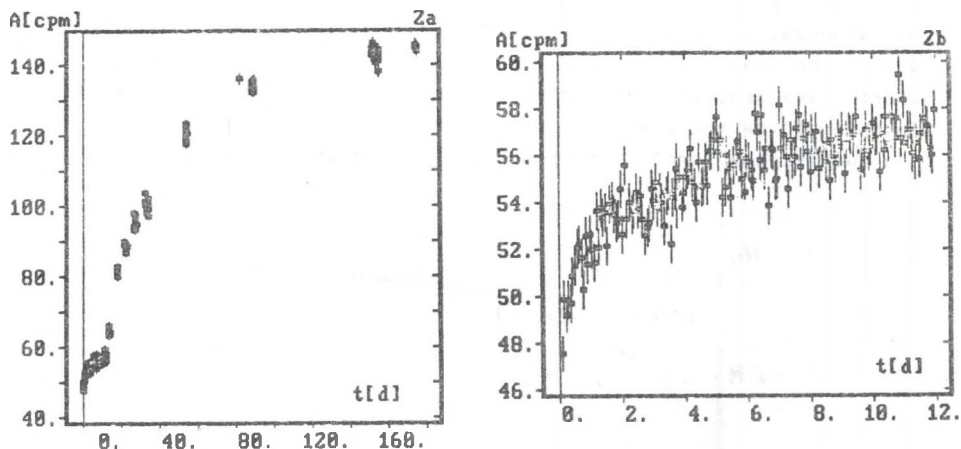


Fig. 2.2a - results of measurements of the increase of radioactivity versus time at 293 K up to 12 days and next at a temperature of 373 K.
2b - enlarged picture of the results at 293 K

Rys. 2.2a - wyniki pomiarów wzrostu radioaktywności w funkcji czasu w temperaturze 293 K w okresie do 12 dni, a następnie w temperaturze 373 K.
2b - powiększony obraz wyników w temperaturze 293 K

The presented results justify the attempt to develop the hypothesis. For further analysis it is advisable to define the density reduction $n(x,t) = (N_0 - N(x,t))/N_0$ instead of the density $N(x,t)$ of the radioisotope as shown in Fig. 1. For $t=0$ n is equal to one for $x=0$ and equal to zero for other values of x . Assuming that the production of the radioisotope is homogeneous in the volume of the material and that the kinetics of the process is affected by diffusion with the diffusion coefficient D and by decay with the mean life time τ , the transport equation takes the following form (see Appendix 1).

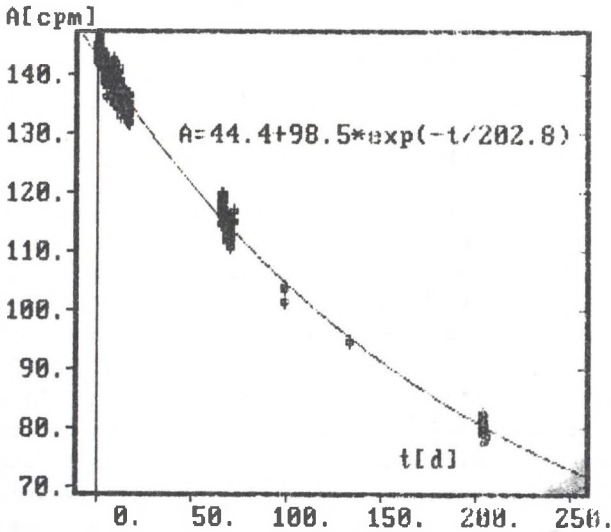


Fig. 3. Decrease of the alpha radioactivity versus time at room temperature, the sample having been brought earlier at a higher temperature to a state of higher radioactivity. The formula is plotted as an approximating curve

Rys. 3. Zmniejszenie alfa - radioaktywności w funkcji czasu w temperaturze pokojowej po wcześniejszym doprowadzeniu próbki do stanu większej radioaktywności w wyższej temperaturze. Na rysunku zapisany jest wzór krzywej aproksymującej wyniki

$$\frac{\partial n(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D \cdot \frac{\partial n(x,t)}{\partial x} \right) - \frac{n(x,t)}{\tau} \quad (2)$$

and the surface density ΔN of the additional polonium atoms on the surface is equal to (Appendix 2)

$$\Delta N(t) = N_0 \cdot \int_0^{\infty} n(x,t) \cdot dx \quad (3)$$

The relative increment of radioactivity is equal to (Appendix 3)

$$\frac{A(t) - A_0}{A_0} = \frac{2}{R} \cdot \left[\int_R^{\infty} n(x,t) \cdot dx + \frac{1}{R} \int_0^{\infty} x \cdot n(x,t) \cdot dx \right] \quad (4)$$

For $t \ll \tau$, the term n/τ can be neglected in equation (2); thus

$$(t \ll \tau) \quad n(x,t) = 1 - \Phi(x/\sqrt{2Dt}) \quad (5)$$

Function Φ is a Laplace integral. This solution can be used as the initial function for the solution of equation (2) by means of iteration. From (5) and (4) we get (Appendix 4)

$$D(x=0) = \frac{R^2}{2A_0} \cdot \left(\frac{\partial A}{\partial t} \right)_{t=0} \quad (6)$$

The values A_0 and $(\partial A / \partial t)_{t=0}$ are approximated from experimental results. The diffusion coefficient of polonium in lead at room temperature evaluated in this way, is of the order of 10^{-12} cm²/s, whereas according to data [5] for bismuth in lead approximated to room temperature (it is believed, that the diffusion of polonium in lead is similar to that at bismuth) is four order lower.

In a steady state ($\partial n / \partial t = 0$) the solution of equation (2) gives for density reduction the dependence $\exp(-x/\sqrt{D \cdot t})$. The increment ΔA of radioactivity calculated this way by means of equation (4) is by one order or more higher than the experimental values. Thus it might be concluded, that the process of strong diffusion occurs only in the layer near the surface at a depth distinctly smaller than the characteristic depth $\sqrt{D \cdot t}$. Consequently this suggests, that the mentioned layer is layer of plastically deformed material in the process of surface scraping. Indeed, lattice defects generated in the process of plastic deformation lead to higher mobilities of the atoms. Such an interpretation suggests, that if the surface layer is removed without plastic deformation, radioactivity should not increase. Such a method is etching. Fig. 4 provides the results of measurements of the sample prepared from another batch of material, first after the scraping of the surface and next after etching. As can be seen, the supposition proves to have been correct.

Because sequence of hypotheses and experimental results is logically consistent, the presented interpretation must be accepted. But then the same should be the case with radioisotope of bismuth. This possibility was mentioned in [4]. The experimental techniques described in [3] and samples stored for two years were used for measurements connected with this problem. First radioactivity alpha was measured and then after the sample had been covered with aluminium foil 11 mg/cm² thick beta radioactivity was measured. The measurements were repeated after the scraping of the sample. In the first two measurements the values $A_0 + \Delta A$ were measured, in the other two only the values of A_0 . In the case of alpha radioactivity the relative change was equal to $190 \pm 6\%$ and in the case of beta radioactivity to $25 \pm 2,5\%$. The latter value is in very good agreement with theoretical calculations by means of equation (4) for bismuth beta particles. The increment of beta radioactivity about one order lower than alpha radioactivity results from the considerably shorter life time of bismuth atoms than polonium and the larger range of beta particles in lead.

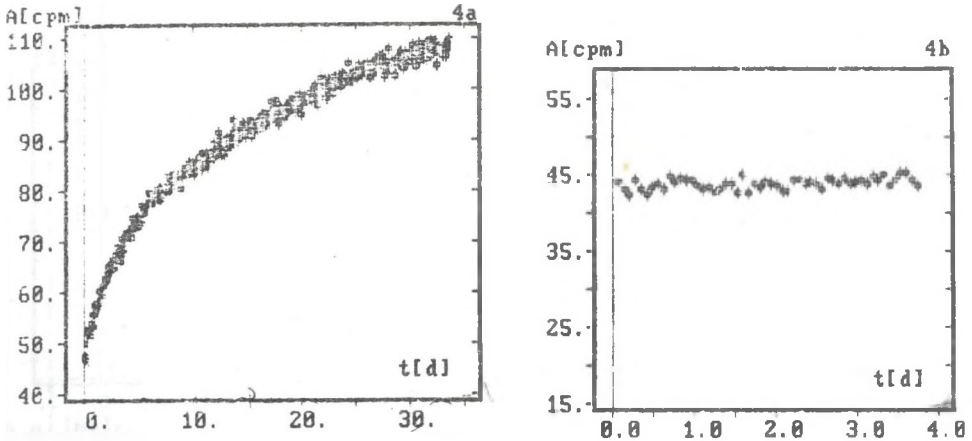


Fig. 4. 4a - Increase of the alpha radioactivity of the sample after scraping at room temperature versus time. 4b - results for the same sample after etching

Rys. 4. 4a - Wzrost alfa-radioaktywności próbki w funkcji czasu skrobania próbki po obróbce w temperaturze pokojowej. 4b - wyniki dla tej samej próbki po trawieniu

If bismuth atoms also participate in the process, equation (2) is valid for bismuth atoms. If n_b and n_p denote the density reduction of the bismuth and polonium atoms respectively, the transport equation for polonium atoms takes the form

$$\frac{\partial n_p}{\partial t} = \frac{\partial}{\partial x} \left(D \cdot \frac{\partial n_p}{\partial x} \right) - \frac{n_p}{\tau_p} + \frac{n_b}{\tau_b} \quad (7)$$

Equation (5) and (6) are still valid.

The diffusion coefficient D should be accepted as the decreasing function versus the coordinate x , analogically as the density of the lattice defects decreases. In order to solve equation (2) and (7) by means of iteration, the diffusion coefficient was approximated by the formula

$$D = D_0 \cdot \left(1 - \frac{x}{L} \right)^m + D_t \quad (8)$$

where the value D_0 was taken from (6) whereas the parameters L and m were determined by successive iteration of equations (2) and (7) for the best agreement of the experimental and calculated results of the radioactivity versus time. The component D_t considers the diffusion coefficient corresponding the thermal equilibrium state. Its value was approximated for room temperature from data for bismuth in lead [5] to $3 \cdot 10^{-16} \text{ cm}^2/\text{s}$.

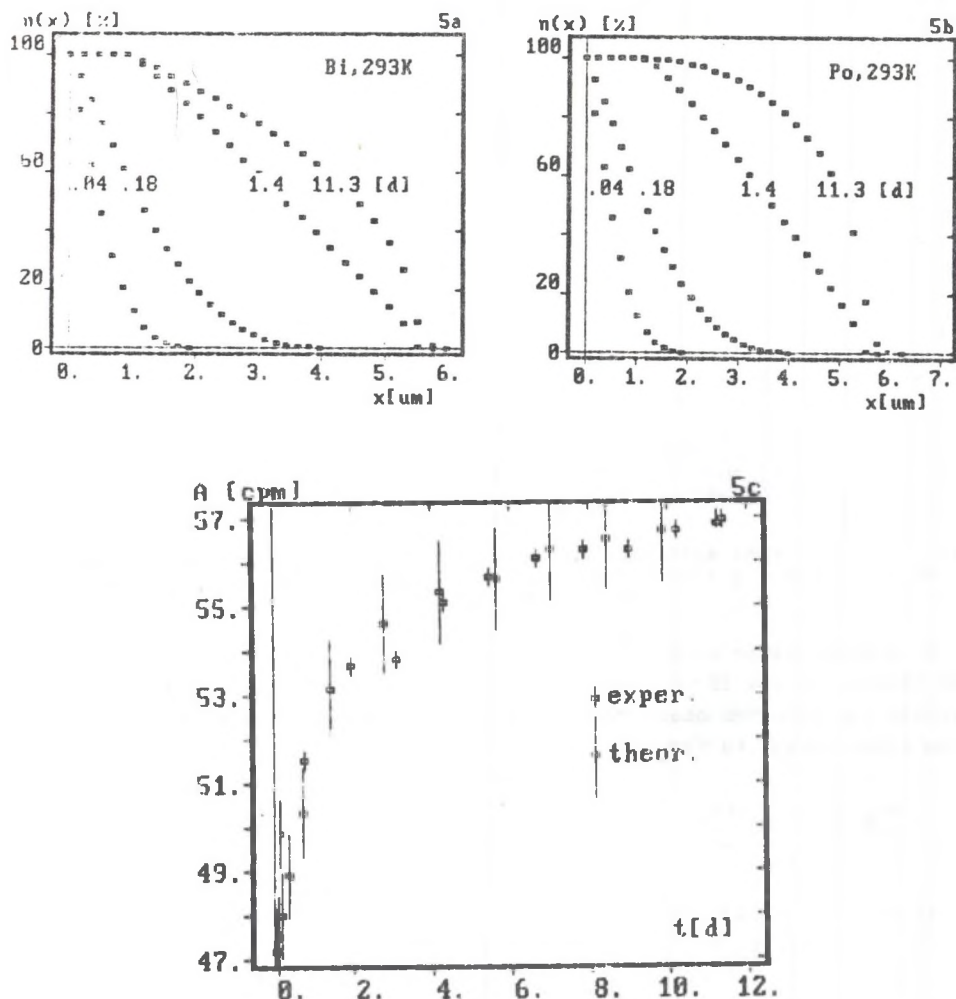


Fig. 5. Results of numerical calculations by means of equations (2) to (8) for the measurements presented in Fig. 2b; $D_0 = 10^{-12} \text{ cm}^2/\text{s}$, $L = 5,5 \mu\text{m}$, $m=1$

5a, 5b - profiles of the density reduction n for bismuth and polonium, at temp. 293 K for several moments of time, 5c - calculated (dots with longer perpendicular dashes) and experimental values of radioactivity versus time. The experimental results are the mean values of the data provided in fig. 2b

Rys. 5. Wyniki obliczeń numerycznych otrzymane przy pomocy równań (2)-(8) dla pomiarów przedstawionych na Rys. 2b; $D_0 = 10^{-12} \text{ cm}^2/\text{s}$, $L = 5,5 \mu\text{m}$, $m=1$

5a, 5b - profile (wykresu) względnego ubytku gęstości n dla bizmutu i polonu w temperaturze 293 K dla kilku wybranych czasów, 5c - obliczone (punkty z dłuższymi pionowymi kreskami) i doświadczalne wartości radioaktywności w funkcji czasu. Wyniki doświadczalne są wartościami średnimi z danych na rys. 2b

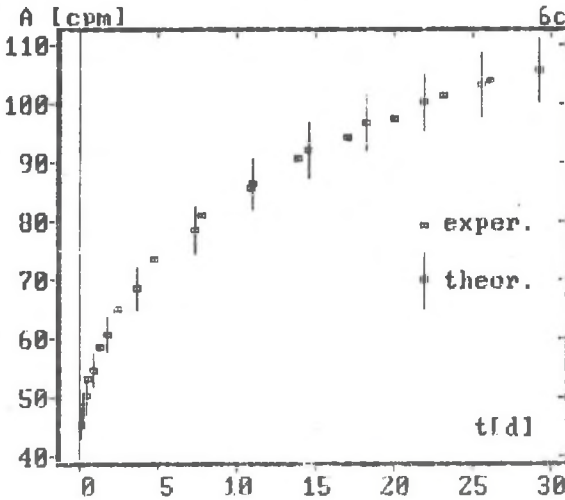
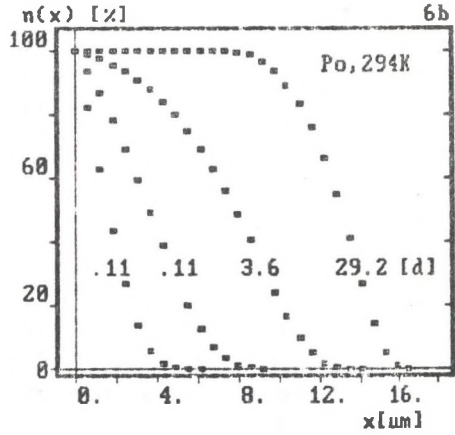
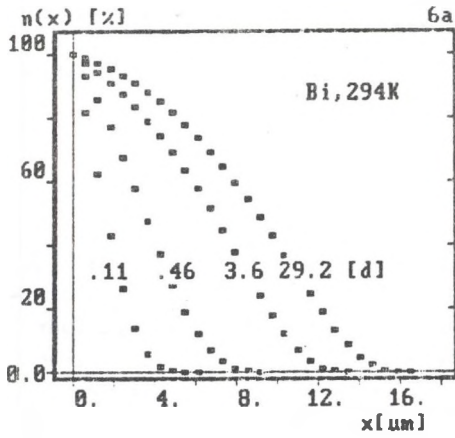


Fig. 6. Results of numerical calculation for the measurements presented in Fig. 4a; $D_0 = 5,2 \cdot 10^{-12} \text{ cm}^2/\text{s}$, $L = 19,6 \mu\text{m}$, $m=5$
 6a, 6b - profiles of the density reduction, 6c - calculated and experimental values of radioactivity

Rys. 6. Wyniki obliczeń numerycznych dla pomiarów przedstawionych na Rys. 4a; $D_0 = 5,2 \cdot 10^{-12} \text{ cm}^2/\text{s}$, $L = 19,6 \mu\text{m}$, $m=5$
 6a, 6b - profile (wykresu) względnego ubytku gęstości, 6c - obliczone i doświadczalne wartości radioaktywności

As examples, the results of such a calculation are shown on Fig. 5 and Fig. 6. The value of D_0 was assumed to be the same for both radioisotopes. This is a simplification which depreciates the value of calculations. It should also be remarked that experimental data are mean values of the sample surface as there was a considerably difference between the cutting speed at the edge of the sample and in its centre part.

Conclusion

From literature (e.g. [6]) we know the phenomenon of the rapid diffusion of some elements in lead in thermal equilibrium. The diffusion coefficients of Cu and Pd, at a temperature of 600 K, for instance, are four orders higher than in the case of self diffusion. But Bi does not belong to these, because its diffusion coefficient in lead is only one order higher [5]. As mentioned earlier, it has been assumed that the diffusion of the polonium is similar to that of bismuth. It has been postulated that the rapid diffusion of these radioisotopes in lead at room temperature is due to the high density of lattice defects generated in the process of plastic deformation near the surface.

In the presented paper the plastic deformation and density of defects have not not been controlled. Experiments with controlled values of those defects might be a source of interesting information about the mechanisms of diffusion affected by lattice defects.

The phenomena described in the present paper may occur in other materials too and may matter in some investigations as well as in practice. **ACKNOWLEDGEMENTS** This work was supported by the Polish Ministry of Education within Project CPBP.01.06, and Committee of Science Investigations. The authors express their gratitude to the Szopienice Non-Ferrous Metal Works for the supply of lead for our investigations.

APPENDIX 1

If $N(x,t)$ denotes the density of the radioisotopes, then the density of its diffusion current is equal

$$i = - D \cdot \frac{\partial N}{\partial x} \quad (D1.1)$$

and the transport equation take the form

$$\frac{\partial N}{\partial t} = \frac{\partial}{\partial x} \left(D \cdot \frac{\partial N}{\partial x} \right) - \frac{N}{\tau} + A_1 \quad (D1.2)$$

The component $-N/\tau$ considers the radioactive decay whereas the term A_1 regards the production rate of the radioisotope. Because in radioactive equilibrium

$$A_1 = N_0/\tau \quad (D1.3)$$

and accepting according to Fig. 1

$$n = (N_0 - N)/N_0 \quad (D1.4)$$

from (D1.2) we arrive at equation (2).

APPENDIX 2

Denoting the surface density of the additional radioisotope on the surface by ΔN , the transport equation for this magnitude takes the form

$$\frac{\partial(\Delta N)}{\partial t} = \left(D \cdot \frac{\partial n}{\partial x} \right)_{x=0} - \frac{\Delta N}{\tau} \quad (D2.1)$$

Considering (D1.4), we have

$$\frac{\partial(\Delta N)}{\partial t} = -N_0 \cdot \left(D \cdot \frac{\partial n}{\partial x} \right)_{x=0} - \frac{\Delta N}{\tau} \quad (D2.2)$$

On the other hand integrating the equation (2) in relation to x from 0 to ∞ we have

$$\frac{\partial}{\partial t} \left(\int_0^{\infty} n \cdot dx \right) = \int_0^{\infty} \frac{\partial}{\partial x} \left(D \cdot \frac{\partial n}{\partial x} \right) \cdot dx - \frac{1}{\tau} \left(\int_0^{\infty} n \cdot dx \right) \quad (D2.3)$$

For $x=\infty$ the values D , n , $\partial n/\partial x$ are equal to zero, so that equations (D2.2) and (D2.3) are equivalent if

$$\Delta N = N_0 \cdot \int_0^{\infty} n \cdot dx \quad (D2.4)$$

APPENDIX 3

From the elementary relations between radioactivity and the density of the radionuclide, taking into consideration the self absorption, we get

$$A(t) = \frac{1}{2\tau} \left(\Delta N(t) + \int_0^R \left(1 - \frac{x}{R} \right) \cdot N(x,t) \cdot dx \right) \quad (D3.1)$$

where R is the range of radiation. Considering equations (1), (D1.4) and (D2.4) we have (4).

APPENDIX 4

Differentiating equation (4) in relation to time we get

$$\frac{\partial A}{\partial t} = A_0 \cdot \frac{2}{R} \left[\int_R^{\infty} \frac{\partial n}{\partial t} \cdot dx + \frac{1}{R} \cdot \int_0^{\infty} x \cdot \frac{\partial n}{\partial t} \cdot dx \right] \quad (D4.1)$$

In the solution of equations (2) and (7) the characteristic value of the length of x , where n is different from zero, is of the order of $\sqrt{D \cdot t}$. If therefore $t \ll R^2/D(x=0)$, the first integral in equation (D4.1) is equal to zero. Then also $t \ll \tau_b$ and the more so $t \ll \tau_p$; thus in equations (2) and (7) the terms n/τ may be neglected. The resulting formula for the derivative $\partial n/\partial t$ can be substituted in (D4.1) and we get

$$\frac{\partial A}{\partial t} = \frac{2 \cdot A_0}{R^2} \cdot \int_0^{\infty} x \cdot \frac{\partial}{\partial x} \left(D \cdot \frac{\partial n}{\partial x} \right) \cdot dx \quad (D4.2)$$

or integrating by parts

$$\frac{\partial A}{\partial t} = - \frac{2 \cdot A_0}{R^2} \cdot \int_0^{\infty} D \cdot \frac{\partial n}{\partial x} \cdot dx \quad (D4.3)$$

Equation (D4.3) concerns small values of time and x because $n=0$ for greater values of x . So the diffusion coefficient D can be replaced by the mean value of D in the respective range of x near zero. Considering that $n(x=0)=1$, we obtain from (D4.3)

$$\text{for } t \ll R^2/\bar{D} \quad \frac{\partial A}{\partial t} = \frac{2 \cdot A_0}{R^2} \cdot \bar{D} \quad (D4.4)$$

In particular, the last formula may be used for $t=0$.

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СЫВКА ДЫФУЗЫА БИЗМУТА И ПОЛОНУ В ОЛОВИУ ДО ПОВЕРЗХНИ,
СТИМУЛОВАНА ПРЗЕС ПЛАСТЫЧНУ ДЭФОРМАЦЮ

S t r e s z c z e n i e

W pracy przedstawia się pomiary oraz ilościową analizę kinetyki zjawiska narastania radioaktywności ołowiu po skrobaniu powierzchni. Wzrost radioaktywności dotyczy radioaktywności alfa polonu oraz w mniejszym stopniu radioaktywności beta bizmutu. Skrobanie powierzchni wywołuje plastyczną deformację warstwy przypowierzchniowej. Generowane defekty uaktywniają dyfuzję bizmutu i polonu do powierzchni, na której potencjał chemiczny tych atomów jest mniejszy aniżeli wewnątrz materiału.

БЫСТРАЯ ДИФУЗИА БИЗМУТА И ПОЛОНИЯ В СВИНЦЕ К ПОВЕРЗХНОСТИ,
СТИМУЛИРОВАННАЯ ПЛАСТИЧЕСКОЙ ДЕФОРМАЦИЕЙ

Р е з ю м е

В статье представлены измерения вместе с количественным анализом кинетики возрастания радиоактивности свинца после сосребывания его поверхности. Рост радиоактивности касается радиоактивности бета висмута. Снятие поверхности пробы ведёт к пластической деформации приповерхностного слоя. Возникшие таким образом дефекты кристаллической сети облегчают диффузию радиоизотопов полония и висмута к поверхности свинца, на которой их свободная энергия меньше чем внутри материала.