IL NUOVO CIMENTO Vol. LII B, N. 2 11 Dicembre 1967

Positron Bound States in Alkali Halides.

C. Bussolati, A. Dupasquier and L. Zappa

Istituto di Fisica del Politecnico - Milano
Gruppo Nazionale di Struttura della Materia del CNR

(ricevuto il 25 Ottobre 1967)

Summary. — The time annihilation spectrum of positrons in alkali halides was investigated by means of high-resolution timing technique. The decay was found to be complex in agreement with previous results. The spectra were consistently resolved in two components and in some cases in three components. The analysis of the whole set of the measured lifetimes and intensities has allowed to gain insight into some peculiarities of the decay; a discussion is given on the basis of a model in which the positron is considered as being bound to a negative ion. By assigning the main components, τ_1 and τ_2, to the annihilation from the ground and first excited levels, the system (anion-e^+) was found to have a size (a few 10^{-8} cm) that makes plausible its existence inside the crystals.

1. – Introduction.

The lifetime spectrum of positrons annihilating in alkali halides was investigated by Bisi, Fiorentini and Zappa (1,2) a few years ago. An outstanding feature of these spectra is their complexity (at least two components were shown) which rules out the old picture of an unique fate for all positrons. On the other hand, the fact that no narrow components have been observed in angular-correlation measurements of the 2 annihilation quanta (3) and additional experimental evidence from three-quantum decay yield (4) exclude

---

(1) A. Bisi, A. Fiorentini and L. Zappa: *Phys. Rev.*, **131**, 1023 (1963).

(2) A. Bisi, A. Fiorentini and L. Zappa: *Phys. Rev.*, **134**, A 328 (1964).

(3) A. T. Stewart and N. K. Pope: *Phys. Rev.*, **120**, 2033 (1960). This article gives references to earlier works.

(4) A. Bisi, C. Bussolati, S. Cova and L. Zappa: *Phys. Rev.*, **141**, 348 (1966).

that a bound state with annihilation characteristics similar to those of the positronium atom is the cause of the long-lifetime component. These results have been interpreted as evidence for the formation of a positron bound system, in which the negative ion plays a predominant role. The nature of such a system is still rather unknown although various hypotheses have been forwarded. GOL'DANSKII and PROKOP'EV (5-7) have proposed three kinds of bound states: *a*) the system anion-e^+, *b*) positron polaron state and *c*) positron bound to crystal defects. BRANDT (8) has examined a model in which the positron is trapped in a vacancy *A*-center. However these suggestions on positron decay in alkali halides must be regarded as merely tentative, owing to the fact that the experimental background was far from being sufficient to draw definite conclusions. Recent improvements in fast-timing techniques have made available further resolution in the time spectra so that one is faced with the necessity of re-examining with greater accuracy the annihilation spectra.

In the present paper we report the results of such an investigation with the aim of getting a more extensive and solid experimental basis for future theoretical work

2. – Experimental procedure.

The positron emitter (^{22}Na from a carrier-free neutral aqueous solution) was deposited on a thin mica foil (1 mg/cm^2); a second identical foil was placed over it and the source so assembled was sandwiched between the specimens under investigation. The specimens were multicrystalline analytical reagent-grade chemicals; in some cases single crystals were used too. The whole process was carried out in a glove dry box and the sandwich source-specimen was enclosed in a hermetically sealed Lucite container.

The measurements of the time annihilation spectra were performed in a conventional way; the experimental set-up has been previously described (9). We shall mention here only that two different sets of timing instrumentation were used; the prompt time resolution curves for the conditions of the present experiment have sides simulating a single exponential decay through at least four decades. The full widths at half maximum are $3.5\cdot10^{-10}$ s and $2.8\cdot10^{-10}$ s respectively and the logaritmic slopes of the sides correspond to a half-life of $6.0\cdot10^{-11}$ s and of $4.5\cdot10^{-11}$ s respectively.

---

(5) V. I. GOL'DANSKII and E. P. PROKOP'EV: *Sov. Phys. Solid State*, **6**, 2641 (1965).

(6) E. P. PROKOP'EV: *Sov. Phys. Solid State*, **8**, 368 (1966).

(7) V. I. GOL'DANSKII and E. P. PROKOP'EV: *Sov. Phys. Solid State*, **8**, 409 (1966).

(8) W. BRANDT: Contribution to the *Proceedings of Wayne Conference on Positron Annihilation* (Detroit, 1965).

(9) C. BUSSOLATI, S. COVA and L. ZAPPA: *Nuovo Cimento*, **50 B**, 256 (1967).

The lifetimes and intensities were obtained after subtraction of the mica contribution according to the procedure indicated by BERTOLACCINI and ZAPPA (10); the analysis of the spectral shape was performed with a maximum-likelihood method which was described in a previous paper (11) and will not be reported here. In addition, a series of exponentials was fitted to the data points by a least-square method; in this case a 7040 IBM computer was used. No significant difference was found in the lifetimes and intensities of the spectral components, arising both from the different operational features of the two timing chains used, and from the two different treatments employed in the data reduction process.

3. - **Results.**

The inspection of the time spectra showed that in some halides a tail accompanied the main components which, if interpreted as arising from an exponential decay, indicates the existence of a long-lifetime (longer than 10^{-9} s) component of faint intensity (lower than 2 percent). Lifetime and intensity of this tail change when passing from multicrystalline to single-crystal specimens while the main components remain unaltered. Hereafter we will not take into consideration this tail and its origin; we wish only mention that powder grains have been found to be responsible of long-lifetime components in various specimens (12,13). However we shall point out that in a few cases of Table I the attribution of the « tail » is questionable.

Figures 1 and 2 show two typical spectra of positrons annihilating in alkali halides, in which two and three components respectively are clearly distinguishable. All the results of our measurements are collected in Table I where the stated errors are conservative estimates and do not arise only from the scatter of experimental results. If one compares these data with those reported in previous papers (1,2), it can be seen that in some cases the agreement is satisfactory, while in other cases a disagreement is evident. This fact can be ascribed mainly to the lower resolution of the old experimental apparatus.

Table I is set up in such a manner as to imply a classification of the different components. Here the indexes 0, 1, 2, 3 individuate the components in order of increasing lifetime; those having the same index should have the same origin. For instance, should we ascribe the various components to the annihilation of positrons from the first levels of a bound system, the same index

---

(10) M. BERTOLACCINI and L. ZAPPA: *Nuovo Cimento* B, to be published.

(11) M. BERTOLACCINI, A. BISI and L. ZAPPA: *Nuovo Cimento*, **46**, 237 (1966).

(12) T. KOHONEN: *Ann. Acad. Sci. Fenn.*, A **6**, 130 (1963).

(13) R. PAULIN and G. AMBROSINO: *Journ. Phys. et Radium*, to be published.

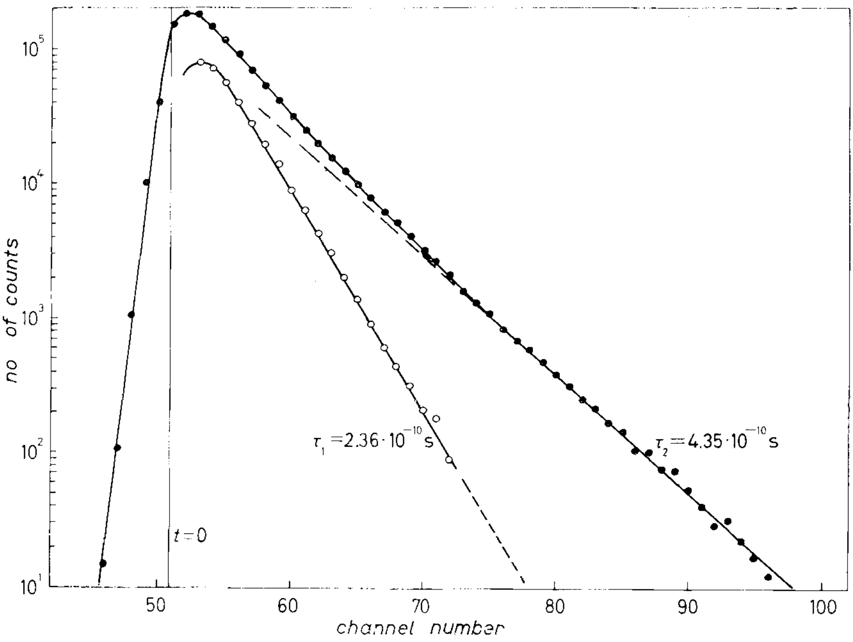

Fig. 1. – Time spectrum of positrons annihilating in LiCl, after subtraction of the tail (1 channel $= 0.88\cdot10^{-10}$ s).

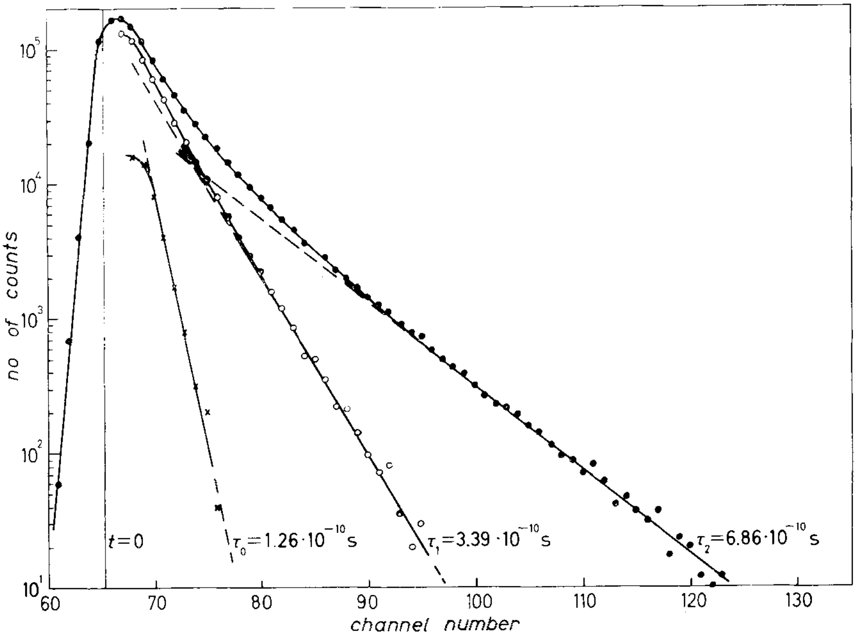

Fig. 2. – Time spectrum of positrons annihilating in CsBr (1 channel $= 1.03\cdot10^{-10}$ s).

TABLE I. – *Mean lives and intensities of positrons in alkali halides.*

Halide	τ_0 (10^{-10} s)	τ_1 (10^{-10} s)	τ_2 (10^{-10} s)	τ_3 (10^{-10} s)	τ_{tail} (10^{-10} s)	I_0 (%)	I_1 (%)	I_2 (%)	I_3 (%)	I_{tail} (%)
LiF	—	1.32 ± 0.07	2.97 ± 0.09	—	11.0; 18.7 (*)	—	31 ± 2	63.1 ± 3.1	—	1.8; 0.4 (*)
NaF	—	1.93 ± 0.10	3.90 ± 0.09	—	36.0; 14.4 (*)	—	27 ± 2	66.0 ± 3.2	—	0.8; 1.3 (*)
KF	—	1.80 ± 0.09	4.24 ± 0.13	10.0 ± 0.3	—	—	34 ± 3	50.0 ± 2.5	9.0 ± 0.2	—
RbF	—	1.55 ± 0.08	3.51 ± 0.11	7.44 ± 0.22	—	—	21 ± 2	61.7 ± 3.1	22.8 ± 0.7	—
CaF	—	1.45 ± 0.08	3.89 ± 0.12	9.38 ± 0.28	—	—	30 ± 3	45.9 ± 2.6	23.9 ± 0.6	—
LiCl	—	2.36 ± 0.12	4.35 ± 0.13	—	17.5	—	51 ± 4	49.1 ± 2.4	—	0.6
NaCl	—	3.13 ± 0.16	6.84 ± 0.20	—	28.9	—	65 ± 5	27.6 ± 0.9	—	1.2
KCl	—	2.75 ± 0.14	6.28 ± 0.19	—	40.5; 24.3 (*)	—	48 ± 4	41.3 ± 2.0	—	1.3; 1.6 (*)
RbCl	—	1.99 ± 0.10	4.56 ± 0.14	10.0 ± 0.3	—	—	27 ± 3	59.3 ± 3.0	7.0 ± 0.3	—
CsCl	—	2.02 ± 0.11	4.51 ± 0.14	12.1 ± 0.3	—	—	42 ± 4	54.6 ± 2.7	5.0 ± 0.2	—
LiBr	—	2.97 ± 0.15	5.56 ± 0.17	—	—	—	79 ± 6	17.1 ± 0.8	—	—
NaBr	—	2.92 ± 0.15	7.46 ± 0.22	—	33.7	—	72 ± 6	16.5 ± 0.7	—	2.0
KBr	—	3.47 ± 0.17	7.55 ± 0.22	—	—	—	64 ± 6	24.2 ± 1.2	—	—
CsBr	1.26 ± 0.09	3.39 ± 0.17	6.86 ± 0.21	—	—	26 ± 3	55 ± 5	22.7 ± 1.1	—	—
LiI	—	3.27 ± 0.17	6.60 ± 0.20	—	—	—	85 ± 7	12.9 ± 0.6	—	—
NaI	—	3.28 ± 0.18	7.76 ± 0.23	—	42.2	—	82 ± 7	10.4 ± 0.5	—	0.8
KI	1.69 ± 0.12	4.01 ± 0.20	7.84 ± 4.54	—	—	17 ± 2	63 ± 5	19.6 ± 0.9	—	—
RbI	1.69 ± 0.12	4.25 ± 0.21	8.05 ± 0.24	—	—	15 ± 1	53 ± 5	24.1 ± 1.2	—	—
CsI	1.83 ± 0.13	3.55 ± 0.20	9.80 ± 0.30	—	—	24 ± 2	70 ± 6	4.0 ± 0.2	—	—

(*) The first number refers to powders, the second to single crystals.

should individuate the same level. At present, however, we do not consider a particular model, but limit ourselves to put in evidence those peculiarities of the decay which have suggested the classification given in Table I. They are:

a) within each series of alkali halides (fluorides, chlorides, etc.) the time spectra display components whose mean life changes slowly by changing the cation;

b) within each series, the components have mean lives which are in a nearly constant ratio (≈ 2.2);

c) this ratio remains nearly constant by passing from one series to another;

d) the τ_1 and τ_2 values, classified as in Table I, show a nearly linear increase with the cube of the negative ion radius. The I_1 values too appear to increase with increasing negative-ion radius. Figures 3 and 4 show these trends for lithium halides.

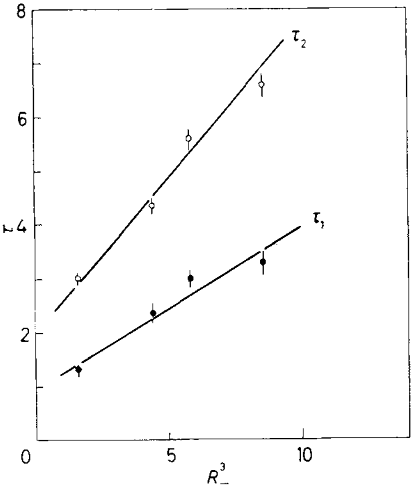

Fig. 3. – Mean lives of positrons in lithium halides as a function of the cube of the negative-ion radius R_-. Units: τ in 10^{-10} s, R_- in 10^{-8} cm.

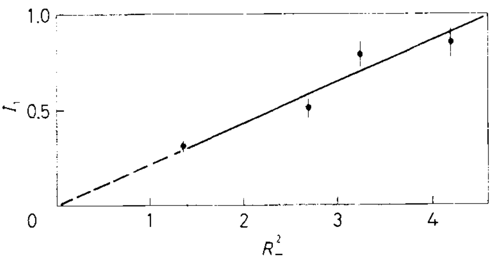

Fig. 4. – Intensity of the τ_1 component in lithium halides as a function of the square of the negative-ion radius R_- (units: 10^{-8} cm).

4. – Discussion.

The results of the previous Section show that the negative ion largely influences the positron lifetimes. On the other hand it is well known from angular-correlation measurements of the 2 annihilation quanta ([3,14]), that the positive

---

([14]) M. King and S. De Benedetti: *Bull. Am. Phys. Soc.*, **12**, 74 (1967).

ion has very little influence on the momentum distribution in comparison with the negative ion. If we assume the formation of an anion-e^+ system having a set of bound levels and ascribe the various time components to the annihilation from the ground and first excited levels, the observation just made and the peculiarities mentioned in the previous Section are framed in an intuitive picture. This model is that suggested for the first time by GOL'DANSKII, IVANOVA and PROKOP'EV (15) for interpreting the positron decay in alkali metal hydrides. In particular the numerical results of GOL'DANSKII *et al.* for the H^--e^+ system show that the ratio between the annihilation lifetimes from successive levels is close to 2.

We will not discuss rigorously the properties of the system anion-e^+, but will limit ourselves to rough considerations with the aim of deducing the size of the system from the observed lifetimes and of comparing it with the lattice constant of the halides. To do that we use a simple model based on drastic assumptions. We consider the positron moving about a core which has an electron configuration like that of a rare-gas atom and represent the potential energy by a series of descending powers of r, neglecting all powers above the second:

$$V(r) = -\frac{\eta e^2}{r} + \frac{c}{r^2}. \tag{1}$$

In eq. (1) $-\eta e$ is the ion charge at infinite distance: c is a constant which is assumed to be positive in order to take into account that the positron, when penetrating through the outer electron shell, experiences the strong repulsive field of the nucleus. c may be expected to depend on the quantum number.

It is a straightforward mathematical problem to solve the Schrödinger equation for the potential (1). The system in a state (ν, l) has the energy

$$E_{\nu,l} = -I_0 \frac{\eta^2}{(\nu + 1 + g)^2},$$

where ν indicates the number of the radial nodes of the wave function; g is given by the equation

$$l(l+1) + \frac{2}{a_0}\frac{c}{e^2} = g(g+1);$$

I_0 and a_0 are the ionization potential of the hydrogen atom and the Bohr radius respectively. The average distance $\bar{r}_{\nu=0}$ of the positron from the nucleus in

---

(15) V. I. GOL'DANSKII, A. V. IVANOVA and E. P. PROKOP'EV: *Sov. Phys. JETP*, **20**, 440 (1965).

the states having $\nu = 0$, becomes

$$\bar{r}_{\nu=0} = \frac{a_0}{2}\,\frac{(1+g)(2g+3)}{\eta}\,.$$

As far as the two-quantum annihilation probability λ is concerned we assume that only the eight electrons occupying the noble-gas configuration are involved; so we get

$$\lambda = 2C_s\int \chi^2(\boldsymbol{r})\,\varphi^2(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}\,, \tag{2}$$

having averaged over spin states of the electron and positron. In eq. (2) C_s is the fundamental interaction rate in the singlet state; $\chi(r)$ and $\varphi(r)$ are the positron and one-electron wave functions for the system. φ may conveniently be represented in the form given by SLATER ([16]):

$$\varphi(r) \simeq r^{n-1}\,e^{-\beta r}\,,$$

where $\beta = (Z-s)/n$; Z is the charge of the ion nucleus, s the screening constant and n the effective quantum number. The explicit expression of the annihilation probability (2) for the states with $\nu = 0$, becomes then

$$\lambda_{\nu=0} = \lambda_p\,\frac{64\pi}{2^{2n}}\,\frac{(2\beta)^{2n+1}}{\Gamma(2n+1)}\,\frac{\{\eta/(1+g)\}^{2g+3}\Gamma(2n+2g+1)}{\Gamma(2g+3)\{\beta+\eta/(1+g)\}^{2n+2g+1}}\,,$$

λ_p being the annihilation probability of the parapositronium ($\lambda_p = C_s/8\pi a_0^3 = 8.0\cdot10^9\ \mathrm{s}^{-1}$). As far as concerns the radiative transition probability from the excited level, it can be expected to be of the optical order of magnitude ($\approx 10^8\ \mathrm{s}^{-1}$), so that it can be neglected as compared with the measured annihilation rate.

We are now able to deduce the unknown values of g for the first two levels ($\nu = 0, l = 0$; $\nu = 0, l = 1$), by using the measured lifetimes and putting $\eta = 1$. However, owing to the roughness of the model, we make the numerical calculation by using the averages of τ_1 and of τ_2 within each alkali series. Table II collects the numerical results.

A check of the results forwarded by our model is provided, in the case of $\mathrm{Cl^-e^+}$, by Simons' ([17]) exact calculation based on the Hartree-Fock self-consistent field. The ground-state energy found by SIMONS was 3.74 eV; thus

---

([16]) J. C. SLATER: *Phys. Rev.*, **36**, 57 (1930).

([17]) L. SIMONS: *Phys. Rev.*, **90**, 165 (1953).

it can be seen that our procedure underestimates the energy by about 30% and consequently over-estimates the size of the system.

At this point and in view of the fact that the anion-e^+ system is contained in a crystal lattice, it is convenient to examine how the numerical results of Table II are sensitive to a change in the effective charge η. For example, still considering Cl^- e^+, a decrease of 20 percent of η gives rise to a decrease of the ground-state energy of about 30 percent and to an increase of the size of only 4 percent. It follows that the size of the bound system depends substantially on the choice of the model and of the form of potential, and not on the effective charge. The size of our systems (Table II) results practically equal to the sum of the anion and cation radii; on the other hand our procedure over-estimates the size, so that the existence of such a bound system within the crystal appears to be plausible, but a more sophisticated model is required for elucidating the role of the positive ion and explaining the small differences observed within each series of halides.

TABLE II. – *Energies and mean radii of the system anion-*e^+ *deduced from the mean lives* τ_1 *and* τ_2. a is the sum of the anion and the cation radii (averaged over the cations in each series).

	$\bar{\tau}_1$ (10^{-10} s)	$\bar{\tau}_2$ (10^{-10} s)	Ground state		First excited state		a (*) (10^{-8} cm)
			E (eV)	$\bar{r}$ (10^{-8} cm)	E (eV)	$\bar{r}$ (10^{-8} cm)	
fluorides	1.61	3.54	3.42	2.62	2.95	2.98	2.58
chlorides	2.45	5.31	2.82	3.11	2.39	3.62	3.06
bromides	3.19	6.86	2.58	3.37	2.20	3.90	3.17
iodides	3.67	8.01	2.43	3.56	2.03	4.20	3.47

(*) The corrected ionic radii are taken from B. S. GOURARY and F. J. ADRIAN: *Solid State Physics*, edited by F. SEITZ and D. TURNBULL, vol. **10** (New York, 1960), p. 127.

Let us now make some considerations about the longest (τ_3) and the shortest (τ_0) component observed in a few cases. If we attempt to discuss these two components within the framework of the assumed model, we are faced with the following two difficulties: *a*) By attributing the τ_3 component to the annihilation from the second excited level ($\nu = 1$, $l = 0$) of the anion-e^+ system and following the previous procedure, one obtains for Cl^--e^+ that the energy of this level is 1.22 eV and its mean radius 8.1 Å. Clearly this size is too large. *b*) The τ_0 component cannot in any way be explained as arising from the same system. Various reasons must be called in to account for these difficulties. Besides the roughness of our model, one could consider the existence of another system into which the anion-e^+ transforms in a rather short time, and moreover the possibility for some positrons to have a fate different from becoming bound to a single negative ion.

RIASSUNTO

Si espongono i risultati dell'analisi di spettri temporali di positoni che annichilano in alogenuri alcalini, ottenuti utilizzando tecniche temporali ad alta risoluzione. Il decadimento è complesso, confermando così precedenti risultati. Gli spettri sono stati risolti in due e in alcuni casi in tre componenti. L'esame di tutti i risultati ha permesso di far luce su alcune peculiarità del decadimento, che vengono discusse sulla base del modello che descrive il positone legato ad uno ione negativo. Attribuendo le componenti principali τ_1 e τ_2 all'annichilazione del livello fondamentale e al primo livello eccitato, si trova che le dimensioni del sistema anione-e^+ sono tali da renderne plausibile l'esistenza entro il cristallo.

Связанные состояния позитрона в щелочных галоидах.

Резюме (*). — Был исследован спектр времени аннигиляции в щелочных галоидах при помощи временной техники высокого разрешения. Обнаружено, что распад является сложным в соответствии с предыдущими результатами. Спектры были последовательно разложены на две компоненты и в каждом случае на три компоненты. Анализ полученных результатов даёт возможность прояснить некоторые особенности распада; проводится обсуждение на основе модели, в которой позитрон рассматривается как связанный с отрицательным ионом. Приписывая основные компоненты, τ_1 и τ_2, к аннигиляции из основного и первого возбуждённого уровней, было найдено, что система (анион-e^+) имеет размеры (несколько 10^{-8} см), что делает возможным существование такой системы внутри кристалла.

(*) *Переведено редакцией.*