

Inert-gas crystals with imbedded impurities

B. M. Smirnov

*I. V. Kurchatov Institute of Atomic Energy, Academy of Sciences of the USSR, Moscow
Usp. Fiz. Nauk 125, 331-349 (June 1978)*

Crystals consisting of atoms of an inert gas (or of gas molecules) and containing imbedded foreign atoms, radicals, or ions are investigated and their parameters are discussed. A review is given of studies of the diffusion of the trapped particles in a given matrix and of the spectroscopic investigations of these particles. An analysis is given of the properties of gas crystals containing imbedded particles at the crystal lattice sites and having long lifetimes at low temperatures.

PACS numbers: 61.55.Dc, 66.30.Jt

CONTENTS

| | |
|---|-----|
| Introduction | 522 |
| 1. Structure of inert-gas crystals with imbedded impurities | 523 |
| 2. Diffusion of imbedded particles in a gas crystal | 524 |
| 3. Experimental studies of imbedded particles in gas crystals | 529 |
| 4. Long-lived gas crystals with imbedded particles | 530 |
| Conclusions | 532 |
| References | 533 |

INTRODUCTION

We shall consider crystals consisting of atoms of an inert gas or of simple molecules (of the type of N_2 or H_2). The coupling between the atoms or molecules in such a crystal is due to the weak attractive van der Waals forces. The energy associated with the attraction between neighboring particles in the crystal is, therefore, small, and such crystals exist only at low temperatures. On the other hand, the separation between neighboring particles exceeds their dimensions. A crystal of this kind, to which we shall refer as a gas crystal, is the most loosely bound material and is found to be the most suitable "filler" in the study of different systems and processes that are difficult to realize in a gaseous medium.

The properties of radicals and intermediate compounds in a given matrix have been extensively investigated in recent years (see, for example, the reviews and monographs by Andrews,¹ Meyer,² Ogden and Turner,³ Hallam,⁴ Barnes,⁵ and Pimentel⁶). These radicals and compounds have long lifetimes because they are frozen into the matrix. Moreover, relatively high radical densities can be achieved in the matrix which, again, ensures that this method of investigating intermediate compounds is very convenient. However, the matrix must have very little effect on the properties of the particles introduced into it, and this means that the most suitable matrix is the gas crystal which has, in fact, been used as a "filler" in such studies.

In addition to investigations of the parameters of radicals and compounds in a matrix, involving studies of the absorption spectra in the optical and infrared, Raman scattering, and electron paramagnetic resonance, matrices of this kind have been extensively used in the study of chemical reactions. Although a matrix in the form of a gas crystal has little effect on the parameters of compounds formed in it, the very presence of the

matrix has a very considerable influence on the kinetics of the processes taking place in its interior. In particular, the low temperature of the matrix and the large number of elastic collisions between the imbedded particles and the atoms or molecules of the matrix lead to the stabilization of the intermediate compounds. The matrix can thus be used to hold weakly bound and metastable compounds that are difficult to produce in the gaseous phase. In a certain sense, therefore, the matrix can be used as an indicator enabling us to establish whether a particular compound can exist. For this reason many chemical compounds were synthesized only in a matrix of this kind. All that has been said refers only to simple chemical compounds.

A metastable crystal consisting of an inert (or molecular) gas with imbedded atoms or radicals may also be of interest for its own sake. In particular, the inert-gas crystal can be used as a medium for storing halogen atoms or atoms of other oxidizing agents. Moreover, the optical and magnetic properties of the atoms or radicals frozen into the matrix may be important for different applied purposes. If the foreign particles are positive or negative ions, the result is a plasma frozen into the matrix, and the electromagnetic or electrical properties of such a system may be of physical and practical interest. An important point is that, although such systems are metastable, their lifetime at low temperatures (of the order of a few tens of degrees) may turn out to be very large, so that they may be regarded as stable systems at such temperatures.

Systems consisting of gas crystals containing imbedded foreign atoms, radicals, or molecules may be divided into two classes. The first class includes those cases where the size of the foreign particle and the parameters describing its interaction with the atoms or molecules of the crystal may be very different from the corresponding parameters for two particles of the gas

crystal itself. The structure of the crystal lattice is then greatly distorted in the region of the foreign particle, and this distortion moves together with this particle. The other situation arises when the parameters describing the interaction of the foreign particle with the crystal particles are similar to those for the interaction between the crystal particles. The foreign particle can then occupy a crystal lattice site, and will only rarely undergo transitions to neighboring sites. Such particles can be retained by the crystal for a very long time. Experimental studies performed so far with gas crystals containing imbedded particles have been concerned mainly with crystals of the first type. Metastable crystals of the second kind are of particular interest because their lifetime may be very large, so that they are practically stable at low temperatures. This, clearly, reveals new possibilities for the application of such objects.

We shall review studies of gas crystals containing imbedded particles and will analyze the properties of such systems with a view to establishing the most promising trends in this area.

1. Structure of inert-gas crystals with imbedded impurities

The particular feature of gas crystals is that the interaction potential between neighboring atomic particles is small in comparison with the characteristic electronic energies, and decreases rapidly with increasing separation between them. The leading properties of the gas crystal are therefore determined by the parameters of the two-body interaction between nearest neighbors. In what follows, we shall briefly examine the problem of the two-body interaction between atomic particles for the range of interaction parameters that is of interest for gas crystals.

Relatively extensive information is now available on the interaction potential between atomic particles in the range in which these particles can form a bond. The most accurate modern method in this area is the analysis of differential cross sections for collisions between the particles. Less accurate values for the two-body interaction potential can be obtained from integrated characteristics, namely, total collision cross sections, transport coefficients (diffusion, thermal conduction, viscosity), the virial coefficients, and so on.

When the separation between the atomic particles is large, so that the interaction potential between them is small in comparison with the characteristic electronic energies, the potential can be determined from the asymptotic theory of interaction between atomic particles and, in the case of interaction between atoms, can be written in the form⁹

$$U = -\frac{C}{R^6} + BR^\alpha e^{-R/\beta}, \quad (1)$$

where R is the distance between the nuclei, the first term corresponds to the van der Waals attraction between the atoms at large distances, and the second term describes the exchange interaction between the atoms,

which is connected with the overlap of their electronic shells. The exchange interaction is a repulsion when the electronic shells of one of the interacting atoms is filled. The expression given by (1) is asymptotically precise in the limit of large separations between the nuclei.

To determine the parameters of metastable gas crystals, we shall use the asymptotic theory of interaction between atomic particles, which is particularly valuable for an arbitrary interacting pair whenever there is a lack of experimental data. It yields more extensive information on the interaction potentials as compared with experiment. We note that the precision of the results obtained from the asymptotic theory is lower than that of the data obtained from measurements of differential scattering cross sections, but is not lower than the precision achieved by other experimental techniques. An important advantage of the asymptotic theory is that it enables us to estimate the accuracy of the final result. For simplicity, we shall henceforth confine our attention to metastable crystals containing only atoms (with noble gas atoms forming the matrix), since the two-body interaction potential then has the simplest form (1) and can be established with the highest precision.

Table I lists the parameters of the interaction potential (1) for typical atomic pairs that may be of interest for the metastable crystals that we are considering. The parameters are expressed in atomic units and are taken from the monograph by Smirnov.⁹ Table I also lists the parameters of the minimum of the potential for the two-body atomic interaction potential, $U(r_m) = -D$, and the separation r_m between the nuclei for

TABLE I. Parameters of the two-body interaction potentials between atoms and of the gas crystal.

| Partners | C, a.u. * | B, a.u. | α , a.u. | β , a.u. | $\frac{D}{10^{-3} \text{ eV}}$ | $r_m, \text{ \AA}$ | $\frac{\delta\alpha}{0,01 \text{ \AA}}$ | $\Delta D/D_1$ | $(R^2/MU)^{1/4}, 0,01 \text{ \AA}$ |
|----------|-----------|---------|-----------------|----------------|--------------------------------|--------------------|---|----------------|------------------------------------|
| Ne-H | 5.7 | 2.1 | 2.15 | 2.26 | 0.85 | 3.6 | 6 | 1.4 | 99 |
| Ne-O | 13 | 1.8 | 2.15 | 2.26 | 5.4 | 2.9 | 3 | 0.01 | 31 |
| Ne-F | 9.1 | 3.4 | 1.94 | 2.39 | 4.1 | 2.9 | 3 | 0.01 | 30 |
| Ne-Ne | 6.6 | 5.1 | 1.78 | 2.52 | 3.8 | 2.8 | — | — | 30 |
| Ne-Mg | 43 | 0.83 | 2.76 | 2.01 | 7.2 | 3.4 | 18 | 0.23 | 28 |
| Ne-Al | 44 | 0.28 | 3.08 | 1.92 | 6.8 | 3.2 | 8 | 0.09 | 31 |
| Ar-H | 20 | 2.5 | 2.38 | 2.08 | 1.7 | 4.0 | 3 | 0.57 | 71 |
| Ar-O | 42 | 2.1 | 2.38 | 2.08 | 8.8 | 3.2 | 6 | 0.07 | 28 |
| Ar-F | 28 | 4.1 | 2.17 | 2.21 | 6.7 | 3.2 | 6 | 0.08 | 28 |
| Ar-Cl | 88 | 4.9 | 2.42 | 2.05 | 12 | 3.4 | 1 | 0.001 | 21 |
| Ar-Ar | 66 | 7.6 | 2.25 | 2.15 | 12 | 3.4 | — | — | 21 |
| Ar-Ca | 250 | 0.54 | 3.27 | 1.75 | 16 | 3.9 | 11 | 0.14 | 23 |
| Ar-Fe | 180 | 1.2 | 2.94 | 1.84 | 16 | 3.7 | 8 | 0.06 | 20 |
| Ar-Ni | 160 | 1.2 | 2.98 | 1.82 | 10 | 4.0 | 12 | 0.30 | 22 |
| Kr-H | 29 | 2.2 | 2.48 | 2.01 | 2.0 | 4.0 | 2 | 0.29 | 82 |
| Kr-O | 56 | 1.9 | 2.48 | 2.01 | 9.2 | 3.4 | 4 | 0.05 | 29 |
| Kr-Cu | 160 | 0.9 | 3.06 | 1.77 | 6.6 | 4.4 | 9 | 0.64 | 24 |
| Kr-Br | 160 | 4.8 | 2.60 | 1.95 | 13 | 3.9 | 8 | 0.10 | 18 |
| Kr-Kr | 130 | 6.1 | 2.45 | 2.03 | 17 | 3.6 | — | — | 16 |
| Kr-Sr | 430 | 0.37 | 3.46 | 1.66 | 14 | 3.8 | 5 | 0.03 | 19 |
| Xe-Li | 410 | 0.28 | 3.66 | 1.57 | 6.2 | 5.2 | 10 | 1.9 | 47 |
| Xe-Ag | 260 | 0.58 | 3.21 | 1.69 | 10 | 4.2 | 7 | 0.28 | 19 |
| Xe-Cd | 320 | 1.1 | 3.01 | 1.76 | 26 | 3.7 | 0 | 0 | 16 |
| Xe-J | 290 | 1.6 | 2.85 | 1.82 | 39 | 3.3 | 13 | 0.08 | 14 |
| Xe-Xe | 260 | 3.8 | 2.71 | 1.89 | 24 | 3.7 | — | — | 14 |
| Xe-Ba | 740 | 0.22 | 3.71 | 1.56 | 28 | 4.0 | 3 | 0.02 | 19 |
| Xe-Hg | 220 | 1.4 | 2.85 | 1.82 | 22 | 3.6 | 3 | 0.01 | 13 |

*a.u. - atomic units

which the minimum occurs. The precision with which these quantities are determined is limited by uncertainties in the atomic parameters in the expression for the exchange interaction potential and by the precision of the approximations employed in the calculation. The overall uncertainty is 20–30% in the case of two interacting inert-gas atoms and roughly 100% in the case of the interaction between an inert-gas atom and some other atom. Many of the results given below must therefore be regarded as only very rough approximations. Since we shall be concerned with qualitative results, we shall not use experimental information on atomic two-body interaction potentials. The most accurate parameters of the interaction potential (obtained by measurements of differential or total scattering cross sections at low energies) are in agreement with the data listed in Table I to within the above limits of error in the case of interactions between two inert-gas atoms,^{10,27} an inert-gas atom and the hydrogen atom,^{28,30} and an inert-gas atom and the oxygen atom.³¹

The structure of the gas crystal corresponds to the case of closest packing, so that the gas crystal with two-body interaction between nearest neighbors is a face-centered cubic crystal.¹⁾ The separation between neighboring atoms in this crystal is practically the same as the separation r_m between two atoms corresponding to the minimum in the two-body interaction potential. If the impurity atom is located at a gas-crystal lattice site, the distance from it to the nearest neighbors will be slightly different from the separation between the neighboring atoms of the inert gas because the equilibrium distance between the impurity atom and the inert-gas atom, r_{1m} , differs from the corresponding r_m for two inert-gas atoms. Consider the distance a_1 between the impurity atom and the nearest inert-gas atom in the gas-crystal lattice, taking into account only short-range order phenomena and assuming that a_1 is not very different from the separation a between the neighboring inert-gas atoms in the lattice. To be specific, we shall suppose that $r_{1m} > r_m$, i.e., $a_1 > a$ ($a \approx r_m$). Next, let us replace an inert-gas atom at the crystal lattice site by an impurity atom. The distance to the nearest neighbors will then increase to a_1 and the separation between neighboring inert-gas atoms that are nearest neighbors will also increase to a_1 and will differ from the equilibrium separation in the crystal $a \approx r_m$. We shall take this effect into account and will determine the optimum separation between the impurity atom and the nearest neighbors from the condition that the total interaction potential between the atoms must be a minimum. Each of the nearest neighbors of the impurity atom has four nearest neighbors among the nearest neighbors of the impurity atom. Hence, by changing the separation between the impurity atom and the 12 nearest neighbors, we have also changed the 24 separations between the nearest neighbors. Since we are near the minima of both interaction potentials, we shall determine the equilibrium distance a_1 between the impurity

atom and an inert-gas atom from the minimum condition for the potential

$$12 \frac{(r_{1m} - a_1)^2}{2} U_1' + 24 \frac{(a_1 - a)^2}{2} U''$$

where U is the interaction potential between two inert-gas atoms and U_1 is the interaction potential between the impurity atom and an inert-gas atom. This gives

$$a_1 - a = \frac{r_{1m} - r_m}{1 + (2U''/U_1')} \quad (2)$$

We have not taken into account the distortion of the lattice at large distances from the impurity atom, so that (2) gives the upper limit for the change in the nearest-neighbor distance, i.e., $\delta a = |a_1 - a|$ (after an inert-gas atom has been replaced by an impurity atom). The values of δa are listed in Table I.

In accordance with the foregoing expressions, the change in the interaction potential between the impurity atom and a nearest-neighbor inert-gas atom as compared with the minimum in the potential of the two-body interaction between the impurity atom and the inert-gas atom is

$$\Delta D = \frac{(r_{1m} - a_1)^2}{2} U_1' = \frac{2(r_{1m} - a)^2 U_1' (U'')^2}{(U_1' + 2U'')^2}$$

This formula is valid for $\Delta D \ll D_1$, where D_1 is the depth of the potential well for the interaction between the impurity atom and the inert-gas atom. Values of this difference are listed in Table I, which also gives the ratio $\Delta D/D_1$ calculated from this formula. The extent to which the condition $\Delta D \ll D$ is satisfied determines the validity of this formula and is a measure of the influence of the impurity atom on the ambient lattice. We shall be concerned in this review with those cases for which this influence is a minimum.

In practice, it may be supposed that, if the change in the distance to nearest neighbors, resulting from the replacement of the inert-gas atom by the impurity atom at the crystal lattice site, is small or comparable with the amplitude of vibration of the impurity atom, the lattice parameters will be unaffected by this replacement. Table I lists values of $(\hbar^2/MU'')^{1/4}$, which is of the order of the amplitude of zero-point oscillations of the nucleus of the impurity atom (M is the mass of the nucleus of the impurity atom and U is the interaction potential). As can be seen, for most of the examples reproduced in the table it can be assumed that the presence of impurity atoms at the sites of the inert-gas crystal lattice does not produce a change in the geometric parameters of the lattice.

The asymptotic theory of interaction between atoms at large separations will therefore enable us to determine the parameters of metastable gas crystal. Such crystals which are the most stable with respect to the displacement of the imbedded atoms contain them at the lattice sites of the crystal. The asymptotic theory of interaction between atoms can therefore be used to identify the most stable of the metastable gas crystals.

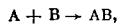
2. Diffusion of imbedded particles in a gas crystal

An important parameter of the metastable gas crystal is the lifetime of the imbedded particles. These

¹⁾We shall not distinguish the face-centered cubic lattice and the closely packed hexagonal lattice: each particle has 12 nearest neighbors in either structure.

particles, which can be atoms or radicals, move through the lattice of the gas crystal and, having encountered one another, form a molecule and, possibly, in time, a separate phase. This process leads to the decay of the metastable state under consideration.

Let us relate the lifetime of the metastable crystal to the parameters characterizing the motion of the imbedded particles in its interior. Suppose that the metastable state decays as a result of the process



where A and B are the impurity particles in the crystal. These particles diffuse through the crystal lattice and react, forming a new compound when they approach one another to a distance r_0 . We shall now derive an equation for the density of particles A , following Smoluchowski.³² The equation for the density $[A]$ of these particles in a region close to a given particle B is $D\Delta[A]=0$, subject to the boundary condition $[A](r_0)=0$. In these expressions, $D = D_A + D_B$, and D_A, D_B are the diffusion coefficients for the indicated particles. The solution of this equation is $[A] = N[1 - (r/r_0)]$, where r is the distance to the given particle B and N is the density of particles A at large distances from the particle B . Hence, we find that the flux of particles A on the test particle B is: $j = -Dd[A]/dr(r_0) = DN/r_0$. If we suppose that the average densities of particles A and B are the same and equal to N , we obtain

$$\frac{dN}{dt} = -4\pi r_0 (D_A + D_B) N^2.$$

The solution of this equation is

$$N = \frac{N_0}{1 + (t/\tau)}, \quad (3a)$$

where

$$\tau = (4\pi r_0 (D_A + D_B) N_0)^{-1} \quad (3b)$$

and N_0 is the density of the imbedded particles at the initial time.²⁾

The lifetime of the metastable gas crystal is thus determined by the diffusion of the imbedded atoms or radicals in its interior. We shall now investigate the nature of the impurity-particle diffusion in the gas crystal, and will estimate the diffusion coefficient for the imbedded particles when they are located at the sites of the crystal lattice. The diffusion coefficient can be estimated from the formula

$$D = D_0 e^{-E_a/T}, \quad (4)$$

where $D_0 \sim a\bar{v}$, a is the separation between the nearest atoms, \bar{v} is the characteristic velocity of an atom in the crystal, T is the temperature in energy units, and E_a is the activation energy for the process under consideration. The factor in front of the exponential is chosen on the assumption that, if the mutual displacement of the atoms were not impeded, the diffusion coefficients could be estimated as for a gas, i.e., $D \sim \bar{v}\lambda$, where \bar{v} is the characteristic velocity of an atom and λ is the mean free path of an atom which, in this case, is

²⁾ This equation and its solution correspond to the case $N_0 r_0^3 \ll 1$.

of the order of a . Table II lists the values of the factor multiplying the exponential in (4), namely:

$$D_0 \sim a \left(\frac{\hbar^2 U_1^*}{M} \right)^{1/4},$$

where M is the mass of the impurity atom and U_1 is the potential of the two-body interaction between the impurity atom and the crystal atom. It is clear that the main problem, in this case, is to determine the activation energy E_a .

The activation energy is determined by the diffusion mechanism (Fig. 1). The most effective diffusion mechanism is connected with the formation of vacancies inside the crystal. The displacement of the impurity atom to a neighboring lattice site is then possible only if there is a vacancy at the latter site. The next displacement becomes possible when the vacancy is formed at one of the neighboring lattice sites. The activation energy is then given by

$$E_a = E_{vac} + E_{tr}, \quad (5)$$

where E_{vac} is the energy necessary for the formation of the vacancy and E_{tr} is the energy necessary for the transition of the atom to the neighboring lattice site at which there is a vacancy.

Let us estimate the activation energy under some simple assumptions. If we take into account only the nearest-neighbor interaction, we find that $E_{vac} = 6D$. In-

TABLE II. Diffusion of atoms in a gas crystal.

| Atom | Crystal | $E_a, 10^{-3}$ eV, from (7) | D_0^* , 10^{-4} cm ² /sec | $T_0, ^\circ$ K |
|------|---------|--------------------------------|---|-----------------|
| O | Ne | 59 | 3.7 | 14 |
| F | Ne | 51 | 3.2 | 14 |
| Mg | Ne | 70 | 3.1 | 14 |
| Al | Ne | 67 | 2.4 | 14 |
| H | Ar | 94 | 28 | 25 |
| O | Ar | 140 | 4.4 | 40 |
| F | Ar | 120 | 3.8 | 34 |
| Cl | Ar | 160 | 2.9 | 46 |
| Ca | Ar | 180 | 2.7 | 46 |
| Fe | Ar | 180 | 2.1 | 46 |
| Ni | Ar | 140 | 2.0 | 40 |
| H | Kr | 130 | 30 | 35 |
| O | Kr | 170 | 4.6 | 48 |
| Cu | Kr | 160 | 1.8 | 46 |
| Br | Kr | 200 | 1.7 | 58 |
| Sr | Kr | 260 | 1.5 | 64 |
| Ag | Xe | 230 | 1.3 | 68 |
| Cd | Xe | 320 | 1.3 | 91 |
| J | Xe | 400 | 1.2 | 91 |
| Ba | Xe | 340 | 0.97 | 91 |
| Hg | Xe | 300 | 0.83 | 89 |

*It is clear from Table II that the exponential in front of the factor in (4) is of the order of 10^{-4} cm²/sec. A more careful analysis of the formation of vacancies and their motion shows that the activation energy is a function of temperature. The values of D_0 deduced from experiment are therefore in the range 0.1–10 cm²/sec for temperatures somewhat less than the melting point of the crystal.³⁷ Since, within the framework of our analysis, this discrepancy between the values of D_0 produces a redefinition of D_0, E_a in (4) which in turn produces an error that lies within the limits of precision that we have adopted, this point can be neglected.

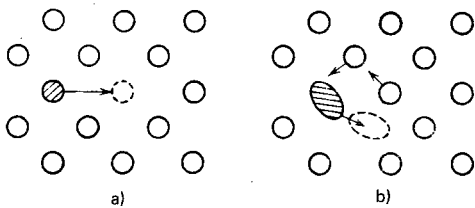


FIG. 1. Two mechanisms for the diffusion of imbedded particles in a gas crystal: a—impurity particle has a size similar to the particles making up the crystal, is located at the crystal lattice site, and its transition to a neighboring site involves the formation of a vacancy and a jump from one site to another; b—the size of the impurity particle is different from that of the crystal particles, so that the crystal lattice is distorted in the neighborhood of the impurity particle and vacancies are more readily produced in this region; the displacement of vacancies near the impurity particle changes the shape of the “cavity” occupied by the impurity particle and its location, and this characterizes the transport of the impurity particle in the interior of the gas crystal.

deed, this represents the energy that must be expended to drive the vacancy from the surface of the crystal into its interior, or the lattice atom from the interior of the crystal to the surface. On the surface, the atom has 6 nearest neighbors whereas, in the interior, it has 12. This means that the energy necessary to form a vacancy in the interior of the crystal is equal to six times the binding energy between two lattice atoms. If we take into account the two-body interaction with the remaining surrounding atoms, and if the two-body interaction potential is taken in the form

$$U(R) = D \left[-2 \left(\frac{r_m}{R} \right)^6 + \left(\frac{r_m}{R} \right)^{12} \right]$$

where R is the separation between the nuclei, the energy associated with the bonding of the crystal atom to the surrounding atom, turns out³⁶ to be $16D$. Accordingly, the energy expended in the formation of the vacancy in the interior of the crystal, i.e., the energy expended in driving the vacancy from the surface to the interior of the crystal, is $8D$. If, on the other hand, the vacancy is formed in the neighborhood of the impurity atom located at a site of the crystal lattice, then

$$E_{\text{vac}} = 7D + D_1,$$

where D, D_1 are the bonding energies between the impurity atom and two and one lattice atoms, respectively.

To determine E_{tr} , we begin by assuming that the transition of the atom to a neighboring free site occurs with the crystal atom remaining stationary. The energy which the imbedded atom must have to undergo the transition to the free neighboring site is equal to the difference between the interaction potential for the given atom and the surrounding atoms when it is located at the lattice site, and when it is located at the midpoint between them. This energy is given by

$$E_{\text{tr}} = 4U_1 \left(a \frac{\sqrt{3}}{2} \right) + 4U_1 \left(a \frac{\sqrt{5}}{2} \right) + 8U_1 \left(a \frac{\sqrt{7}}{2} \right) + 2U_1 \left(\frac{3}{2} a \right) - 11U_1(a) - 2U_1(a\sqrt{2}) - 4U_1(a\sqrt{3}) - U_1(2a); \quad (6)$$

where U_1 is the interaction potential between the given atom and the surrounding atoms and the argument indicates the distance between the nuclei for which the potential is evaluated. In deriving this expression, we

took into account only the interaction with atoms that are the nearest neighbors in relation to one of the sites involved in the transition of the test atom. Moreover, the nuclei are here regarded (and will continue to be regarded) as classical particles, i.e., it is assumed that the energy of zero-point oscillations is small in comparison with the depth of the interaction potential $[\sqrt{\hbar^2 U''/M} \ll D]$.

In view of the very approximate nature of our calculations, we shall approximate the two-body interaction potential between the atoms by the most usable model, namely,

$$U_1 = -D_1 \left[2 \left(\frac{r_m}{R} \right)^6 - \left(\frac{r_m}{R} \right)^{12} \right],$$

where R is the separation between the nuclei. If we use this expression in (6), we find that $E_{\text{tr}} = 9.2D_1$. This is, clearly, too high, since the displacement of the test atom is accompanied by a shift of the neighboring atoms away from their normal positions and, since the interaction potential is very sensitive to changes in separation, this will reduce the height of the barrier. The error can be reduced to some extent by taking this effect into account, but only for the four nearest neighbors of the displaced atom, which are the nearest neighbors both for this atom and for the vacancy. At the midway point, the distance from the displaced atom to the stationary atoms is $a\sqrt{3}/2$. Let us shift these lattice atoms when the displaced atom is at the half-way point along its path, and take into account the interaction of these atoms only with their nearest neighbors. We then find the optimum shift of these lattice atoms from the condition for the minimum of total interaction energy.³⁾ The final expression for the energy necessary for the displacement of the imbedded atom to a neighboring available vacancy is $E_{\text{tr}} = 4.8D_1$. According to (5), the activation energy for the diffusion process is then

$$E_a = 7D + 6D_1, \quad (7)$$

where D is the dissociation energy of the molecule consisting of two lattice atoms and D_1 is the bonding energy between the imbedded atom and the lattice atom. Table II lists values of the activation energy corresponding to the diffusion process for a number of atoms in inert-gas crystals. They were calculated from (7).

The method discussed above of calculating the activation energy for the diffusion process is presented here because of its graphic and simple nature. Among the existing theoretical calculations of activation energy^{33-35, 37} many take into account more accurately the connection between the activation energy and the poten-

³⁾ This corresponds to the minimization of the following sum of interaction potentials:

$$U_1 \left(\frac{\sqrt{3}}{2} (a + \delta) \right) + \frac{1}{2} U_1(a + \delta) + 2U_1 \left(a + \frac{\delta}{4} \right) + 2U_1 \left(a - \frac{\delta}{4} \right) + 2U_1 \left(a - \frac{3\delta}{4} \right) + U_1 \left(a - \frac{\delta}{2} \right) + \frac{17}{2} D_1.$$

The quantity $\delta \ll a$ characterizes the shift of the atom under consideration and $\delta = 0$ corresponds to the condition given by (6) when the lattice atoms remain stationary during the displacement of the imbedded particle.

tial of interaction between atoms, with the accuracy of obtaining the activation energy for the diffusion process being determined by the accuracy of the pair interaction potential for the atoms in the crystal. In all these calculations the activation energy for diffusion processes is comparable with the energy of sublimation which for the chosen form of the interaction potential between the atoms³⁶ amounts to $8D$. We note that for other diffusion mechanisms which do not involve the formation of vacant sites in the crystal the activation energy for the diffusion process is greater than that given by Eq. (7). In particular, in the absence of vacant sites the most effective diffusion mechanism is associated with a cyclic permutation of three atoms which are each other's nearest neighbors. If we neglect the interaction between these atoms in the course of their moving to new positions then the activation energy for this process will exceed $2E_{tr} + E_{tr}^{(1)} > 10D + 5D_1$, and this is somewhat higher than the value corresponding to Eq. (7).

The experimental methods for measuring the activation energy for self-diffusion in a gas crystal are based on studies of isotopic exchange with the vapor above the crystal surface. Table III shows the experimental data and the results obtained from (7), as well as those calculated from the semiempirical formula of Oshcherin.⁴³ This formula can be obtained as follows. Let us suppose that the transition of the imbedded atom to a neighboring free lattice site is accompanied by a small displacement of a large number of ambient atoms. The activation energy for the diffusion process is then given by $E_a \sim a^2 U''$, where a is the lattice constant and U is the two-body interaction potential between the atoms. Since, by definition of the Debye frequency ω_D , $U'' \sim M \omega_D^2$ for a crystal with the two-body interaction (M is the mass of a crystal atom), it follows that⁴³

$$E_a = 0.029 M \omega_D^2 a^2, \quad (8)$$

where the numerical coefficient is chosen so as to ensure the best fit to the experimental data.

The formation of vacancies in the crystal is a special problem. Experiment shows that the concentration of vacancies is small even near the melting point. Thus, it has been established⁴⁴ that the concentration of vacancies in solid argon is less than 0.0037, whereas the value near the melting point⁴⁵ is less than 0.0025. Studies of solid krypton have shown⁴⁶ that the concentration of vacancies in this material is less than 0.001. Particularly careful studies of solid krypton⁴⁵ have shown that the concentration of vacancies at the melting point is 0.003. Moreover, it was found that the energy of formation of vacancies is two-thirds of the sublimation energy. We note that we have assumed in the derivation

TABLE III. Activation energy for the self-diffusion of atoms in inert-gas crystals (0.01 eV).

| Crystal | Debye frequency, ³⁷ 10 ¹² sec ⁻¹ | Experiment | Equation (7) | Equation (8) |
|---------|--|---|-----------------|-----------------|
| Ne | 8.6 | 4.1 ± 0.2 ^[41] | 4.9 | 3.5 |
| Ar | 11 | 17 ± 1 ^[39] ; 16 ± 1 ^[38] | 16 | 17 |
| Kr | 8.4 | 21 ± 1 ^[40] ; 22 ± 1 ^[63] | 22 | 23 |
| Xe | 7.2 | 32 ± 0.2 ^[42] | 31 | 28 |

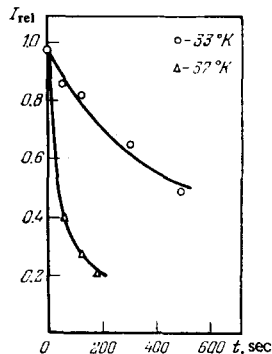


FIG. 2. Relative absorption of $\text{Ag}(\text{CO})_3$ in solid CO as a function of time in the infrared absorption band.⁵⁰ The temperature of the solid CO is 33°K and 37°K.

of (7) that these two quantities are equal.

There are as yet no reliable methods for the precise determination of the diffusion coefficients for foreign atoms and molecules in a gas crystal. Very few such measurements have been carried out and have yielded only the order of magnitude for the diffusion coefficient. The measurements were based on an analysis of (3), which gives the density of imbedded particles as a function of time. This method was used to determine the diffusion coefficient for CO molecules in solid argon⁴⁸ and for Sn atoms in solid nitrogen.⁴⁹ In both cases, the diffusion coefficient at 30°K was of the order of 10^{-16} cm²/sec. Figures 2 and 3 show the results of measurements of the diffusion coefficient for $\text{Ag}(\text{CO})_3$ in solid CO.⁵⁰ The diffusion coefficient was found to vary from 10^{-18} to 10^{-15} cm²/sec when the temperature was varied from 30 to 37°K. The activation energy for the diffusion of this molecule was found to be 1.9 ± 0.3 kcal/mole or 0.082 ± 0.0013 eV. Equation (8) yields the figure of 0.72 kcal/mole for the activation energy of this process.

It is important to remember that the diffusion of imbedded atoms, molecules or radicals in a gas crystal is substantially facilitated if the dimensions of these particles and the parameters of their interaction with the atoms or molecules of the crystal are very different from the corresponding parameters for the lattice particles. When this is so, the imbedded particle produces a substantial distortion of the lattice in its own neighborhood, and this facilitates the displacement of the neighboring crystal atoms and, consequently, of the

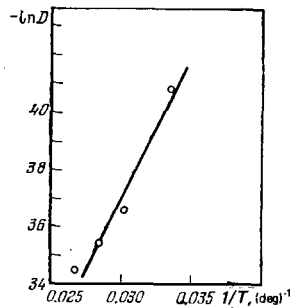


FIG. 3. Logarithm of the diffusion coefficient in solid CO as a function of the reciprocal temperature.⁵⁰ The activation energy for this diffusion process is 1.9 ± 0.3 kcal/mol.

imbedded particle itself (Fig. 1b). The lowest values of the diffusion coefficient correspond to the case investigated above, where the imbedded particle is at the crystal lattice site and its diffusion involves displacement over the crystal lattice sites.

We shall now estimate the lifetime of a number of metastable crystals of this type in order to confirm the reality of their existence. We shall suppose that $r_0 = a$ in (3), i.e., we shall assume that, if they find themselves on neighboring crystal lattice sites, the imbedded atoms automatically recombine. Since $N_0 = (\sqrt{2}/a^3)c$, where c is the concentration of the impurity atoms, the formula given by (3b) can be rewritten in the form

$$\tau = \frac{\tau_0}{c}, \quad \tau_0 = \frac{a^2}{4\pi\sqrt{2}(D_A + D_B)}. \quad (9)$$

Table II lists values of the crystal temperature T_0 for which the lifetime τ_0 is of the order of a day within the framework of this particular model. These parameters are defined with an uncertainty of 100%. We note that since, in practice, the impurity concentration in a given crystal may be much less than 1%, $\tau \sim 1$ day corresponds to a crystal lifetime of the order of or much greater than a week. The analysis thus shows that metastable crystals are practically stable at low temperatures.

The results listed in Table II are in approximate correspondence with Pimentel's rule of thumb.⁶ Essentially, this rule states that imbedded particles in a gas crystal can remain isolated for a fairly long time only if the crystal temperature is less than half the melting point.⁴⁾

It is important to note one further feature of the diffusion of imbedded particles in a metastable gas crystal at low temperatures. A crystal of this kind will always contain impurities which considerably distort the lattice and facilitate the appearance and transport of vacancies. At very low temperatures, when the concentration of vacancies in the crystal becomes comparable with the concentration of such impurities, these impurity centers will influence the formation of vacancies in the crystal and, consequently, the displacement of particles in its interior. The diffusion coefficient for the imbedded particles in a gas crystal at low temperatures therefore depends on the purity of the crystal. The imbedding of impurities distorting the lattice in the gas crystal will then facilitate and increase the diffusion coefficient for the imbedded particles in the crystal.

An increase in temperature leads to the decay of the metastable gas crystals. On the other hand, recombination of foreign atoms inside the crystal is accompanied by the release of heat, and may accelerate the crystal decay process. It is, therefore, meaningful to consider the stability of a metastable gas crystal against thermal explosion,^{7,8} i.e., an unstable process in which the heat

release is so great that the liberated energy does not succeed in leaving the crystal and produces explosive heating. We shall derive the criterion for thermal instability for the simplest geometry in which the specimen is in the gap between two infinite plates held at a temperature T_w . The temperature of the specimen at its center is T_0 and the distance between the center and the walls is l . The heat release in the interior of the specimen is due to the recombination of foreign atoms or radicals, and is determined by their diffusion in the crystal. In accordance with (4), the heat release per unit volume per unit time will therefore be written in the form $A \exp(-E_a/T)$, where A is a slowly-varying function of temperature. The heat is lost from the specimen as a result of thermal conduction, so that the equation for the temperature is

$$\kappa \frac{d^2T}{dx^2} + A e^{-E_a/T} = 0,$$

where κ is the temperature diffusivity and the x axis is perpendicular to the two plates.

Since the heat release occurs only in the neighborhood of the center, we obtain $T(x) = T_0 - \kappa \Delta T/l$, where $\Delta T = T_0 - T_w$. Next, integrating this equation with respect to x , we find that the relation between the temperature at the center of the specimen and on the walls is

$$\Delta T = \frac{T_0 l \sqrt{A}}{\sqrt{E_a \kappa}} e^{-E_a/2T_0}.$$

Let us consider this in greater detail. The right-hand part of this relation is a more rapidly-varying function of temperature at the center than the left-hand part. If the derivative of the right-hand part with respect to T_0 is greater than unity for $\Delta T = 0$, this formula is not satisfied for any T_0 . This means that, in fact, thermal conduction will not ensure the removal of the heat released in the interior of the specimen. The criterion for thermal instability in the case of this geometry is, therefore,

$$\frac{E_a l^2 A}{4T_0^3 \kappa} e^{-E_a/T_0} < 1.$$

Estimates performed for a number of metastable gas crystals have shown that, in practice, thermal instability does not produce a substantial restriction on the region of existence of such systems. As an example, Table IV shows T_{crit} for an argon crystal containing chlorine atoms. If the temperature on the surface of the crystal is greater than T_{crit} thermal instability, leading to fast recombination of the chlorine atoms, develops inside the specimen. Comparison with Table II shows that, for realistic values of the parameters of the specimen,

TABLE IV. Critical temperature corresponding to the thermal instability of an argon crystal with imbedded chlorine atoms.

| cl *) | 0.001 | 0.01 | 0.1 | 1 | 10 | 100 |
|------------------|-------|------|-----|----|----|-----|
| T_{crit} , deg | 80 | 65 | 57 | 50 | 45 | 40 |

*) c —concentration of chlorine atoms in %, l —linear size of the specimen, cm.

⁴⁾ The melting point for inert-gas crystals is as follows⁵¹: 24.2°K for neon, 84°K for argon, 116°K for krypton, and 161°K for xenon.

this quantity exceeds the temperature that ensures a sufficiently slow recombination of the atoms.

3. Experimental studies of imbedded particles in gas crystals

We begin by considering the methods available for producing gas crystals with imbedded particles. There is a number of them. The most widely used method is based on the implantation of the atoms or radicals directly in the interior of the crystal. This is done by adding stable molecules to the gas during the formation of the gas crystal by deposition on a cold surface. These molecules are then exposed to radiation which produces radicals or atoms in the interior of the crystal. For example, the radical XeF was produced in a neon matrix⁵² at 4 °K by freezing a mixture consisting of CF₄, Xe, and Ne in a ratio of 1:5:1000. Ultraviolet radiation was then used to produce partial photodissociation of CF₄ with the formation of the fluorine atom. This atom has a relatively high initial energy and moves through the interior of the crystal. It has a finite probability of encountering a xenon atom and thus forming the radical XeF, which is to be investigated.

The disadvantage of this method is that it also produces foreign radicals (in this example, CF₃) which, at low temperatures, will influence the formation of vacancies in the gas crystal and, consequently, the lifetime of the imbedded particles in the crystal. However, the method turns out to be very convenient when simple molecules are used to produce the radicals. For example, to produce solid argon with imbedded chlorine atoms, it is convenient to prepare the condensed mixture of argon and molecular chlorine and then expose it to ultraviolet light. The chlorine molecule then splits into chlorine atoms which have sufficient energy to travel through the crystal lattice and are eventually trapped at the lattice sites.

The other method of producing a gas crystal with imbedded particles is to prepare the foreign particles in the form in which they are required in the matrix. This is so in all cases where the impurity particles are metal atoms. The most convenient method of producing these atoms is based on the use of the Knudsen cell.^{2, 6} This cell is a closed container made of a high-melting metal with a narrow aperture. It is loaded with the metal under investigation and heated. When the temperature is high enough, the vapor of the metal effuses through the aperture and this directional beam of atoms is intercepted by the target on which it condenses together with the gas whose particles make up the gas crystal. This method can be used to produce a gas crystal with a regulated concentration of imbedded particles.

Although the above methods of producing gas crystals with imbedded particles are the most practical, there are several other approaches. For example, the impurity atoms or ions can be introduced into the gas crystal by bombarding it with these atoms or ions. Since each particle transports relatively large amounts of energy which is eventually used up in heating the crystal, and produces a number of crystal defects, this

TABLE V. Parameters of the radical C₂⁻ (in cm⁻¹).

| Matrix | | Gaseous phase | N ₂ ⁵⁴ | Ne ⁵⁵ | Ar ⁵⁴ | Kr ⁶⁵ | Xe ⁶⁵ |
|--------------------------|--|---------------|------------------------------|------------------|------------------|------------------|------------------|
| Electronic ground state | Energy of vibrational quantum, | 1781.0 | 1792.2 | 1801.2 | 1803.6 | 1797.8 | 1783.8 |
| | Anharmonism, ω _e X _e | 11.6 | 11.5 | 16.7 | 12.1 | 11.6 | 11.0 |
| Excited electronic state | Energy of excitation of the electronic state, T _e | 18391 | 19023 | 18726 | 19109 | 19054 | 19106 |
| | Energy of vibrational quantum, ω _e | 1968.7 | — | 1937.3 | 1986.2 | 1970.4 | 1967.2 |
| | Anharmonism, ω _e X _e | 14.4 | — | 22.6 | 18.2 | 16.5 | 14.6 |

approach is only suitable for very low currents and concentrations of foreign particles in the gas crystal.

Crystals with imbedded radicals are widely used at present to investigate the properties of radicals. Such studies are based on various methods. Investigations of Raman scattering and the infrared absorption spectrum of radicals can be used to establish their vibrational parameters, whereas the absorption spectrum of a radical frozen into the matrix yields information on the parameters of its electronically excited states. Finally, electron paramagnetic resonance can be used to establish the presence of chemical bonding involving the participation of the radical under investigation.

We shall not pause to consider the results of such studies in detail and will merely note their leading features. The main conclusion of these investigations is that the parameters of the radicals frozen into the matrix are not very different from the parameters in vacuum. The interaction between the imbedded radicals and the atoms or molecules of the gas crystals is weak and has little effect on the individual properties of the radicals. As a demonstration of this, Table V lists the parameters of the ground and electronically excited states of the radical C₂⁻ in the gaseous phase and in different gas crystals. Table VI gives the parameters of the ground and electronically excited states for the radicals XeF and KrF, for which the potential curves are shown in Fig. 4. Table VII gives the mean vibration frequencies for a number of carbonyls in different matrices. The relatively slight dependence of the parameters of the radicals on the type of matrix suggest that

TABLE VI. Parameters of electronically excited states of the radicals XeF, and KrF (in cm⁻¹).⁵⁶⁻⁵⁹

| Radical | | XeF | | | KrF | | | |
|------------------|---|--|-------|-------|-------|-------|-------|-------|
| Matrix | | Gas | Ne | Ar | Gas | Ne | Ar | |
| Electronic state | B | Energy of excitation of the electronic state | 28800 | — | 24900 | 40100 | 39900 | 37800 |
| | | Energy of vibrational quantum | 309 | — | 280 | 341 | 340 | 315 |
| | D | Energy of excitation of electronic state | 38100 | 37670 | 35900 | 47100 | — | 43000 |
| | | Energy of vibrational quantum | 350 | 340 | 316 | 356 | — | 336 |

TABLE VII. Mean vibrational frequencies excited in infrared absorption by molecules (in cm^{-1}).^{60,61}

| Molecule | Matrix | | | | |
|---------------------|--------|------|------|------|------|
| | Ne | Ar | Kr | Xe | Gas |
| AgCO | — | 1958 | 1951 | 1945 | 1966 |
| Ag(CO) ₃ | — | 1955 | 1933 | 1926 | 1975 |
| Au(CO) ₂ | 1929 | 1923 | 1917 | 1910 | 1913 |

investigations of the properties of radicals in matrices will, within limits, establish the individual properties of these radicals in vacuum.

This means that studies of radicals in matrices are capable of yielding extensive information on the properties of the radicals. In particular, they have established the existence of radicals such as XeCl and XeBr.^{57, 62} Studies performed in matrices have resulted in values for the parameters of the electronically excited states of the radicals KrF, XeF, OH, NH, C₂⁻, CF₂, and others.^{52, 54-57, 63-70}

Experiments with matrices are also important from the point of view of establishing the existence of various simple chemical compounds. The conditions under which chemical reactions take place in a gas crystal are different from those in the gaseous phase. The interaction with the surrounding particles of the gas crystal enables one to perform reactions of the form $X + Y \rightarrow XY$, which, in the gaseous phase, are only possible in ternary collisions. This fact and the low temperatures of the crystal ensure that whole groups of chemical compounds can be obtained in matrices but, because of their low stability, have never been observed in the gaseous phase. They include, in particular, such compounds as MO₂ (M = Li, Na, K, Ca, Sr, Ba, Ni, Pd, Pt),⁷¹⁻⁸⁰ MO₄ (M = Na, K, Rb, Cs, Cr, Ni, Cu, Pd, Au, Pt),^{76, 79, 81-83} MO₃ (M = Li, Na, K, Pb, Cs),⁸⁴ M(CO)_n (M = Ni, Cu, Ag, Au, Ta, U),^{80, 61, 85-87} M(N₂)_n (M = Ni, Pd, U),⁸⁸⁻⁹¹ and so on.

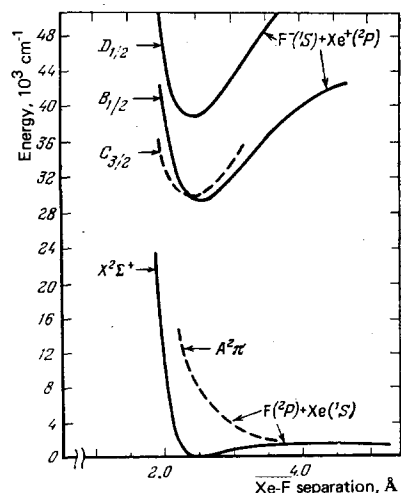


FIG. 4. Potential curves for the radical XeF. The lower terms X, A correspond to ground state of the interacting atoms, and upper terms B, C, D are formed with the participation of ionic states.

Investigations of the properties of radicals in gas crystals have thus yielded extensive information on the parameters of these radicals, on the relatively unstable chemical compounds which can be formed with the participation of the radicals, and on the properties of these compounds. All this has stimulated the development of methods for the investigation of atoms, radicals, and molecules in gas crystals, and has resulted in a reliable experimental base upon which such objects can be obtained and investigated. In my view, the most interesting development is the production of metastable gas crystals in which the imbedded atoms, radicals, or ions are at the sites of the crystal lattice.

4. Long-lived gas crystals with imbedded particles

We shall now consider a gas crystal with imbedded atomic particles in which the size of the impurity particle is similar to that of the atoms or molecules making up the crystal. The imbedded particle is in this case "stuck" at a site of the crystal lattice and the system may exist for a long time at low temperatures. This opens up new possibilities for the use of metastable gas crystals.

Let us consider some special cases of such objects and the ways in which they can be used. One such metastable crystal can be obtained by introducing chlorine atoms into solid argon or oxygen or fluorine atoms into solid neon or argon. At low temperatures, these atoms will remain in the solid matrix for long periods of time, so that the metastable crystal under investigation may subsequently be used as a source of the impurity atom which can be released by heating. This type of metastable crystal can thus be used as a method of storing highly reactive atoms.

Another example of a metastable gas crystal of this kind can be obtained by adding calcium, iron, or nickel to condensed argon, or mercury or thallium to condensed xenon, and so on. A system of this kind is of considerable interest in two respects. On the one hand, it acts as an optical filter, absorbing radiation in narrow bands near the absorption lines of the impurity atom. It can also be used as a laser operating between the states of the impurity atoms whose levels are slightly broadened and shifted by the interaction with the ambient atoms or molecules. If, at the same time, we use magnetic impurity atoms, i.e., atoms with non-zero spins, the magnetic properties of the system become physically interesting.

We note that, in each of the above cases, the impurity acts as a gas of atoms dissolved in the condensed inert or molecular gas. The density of the impurity atoms can be very high. Thus, for impurity concentrations of, say, 0.1% in solid argon (in practice, one may well consider impurity concentrations much less than 1%), the density of impurity atoms is about $4 \times 10^{19} \text{ cm}^{-3}$. This corresponds to a pressure of the gas atoms at room temperature exceeding 1 atm.

The system consisting of solid xenon and containing positive cesium ions and negative iodine ions, or solid argon with added positive potassium ions and negative

chlorine ions, are examples of the most interesting type of metastable crystal of the kind considered above. Here, we have a peculiar form of plasma which efficiently absorbs microwave radiation or can be a source of this radiation at frequencies of the order of the plasma frequencies. Moreover, the plasma density can be quite high in comparison with the gaseous system. At the same time, in contrast to the gaseous system, it is possible to produce inhomogeneous layers of imbedded particles, which enhances practical interest in this type of system. Let us consider such systems in greater detail.

The presence of ions in gas crystals has been demonstrated by a number of experiments. For example, Li^+ and OF^- ,⁹² UO_2^+ and NO_3^- ,⁹³ NH_4^+ and NO_3^- ,⁹⁴ H_3O^+ and NO_3^- ,⁹⁴ and so on have been investigated in the argon matrix at low temperatures. The presence of the positive and negative molecular ions in the matrix was established from their vibrational spectrum, since the vibrational spectra of the ions and of the corresponding neutral particles are quite different. In all these cases, the size of the ions is large enough and they can undergo appreciable displacement in the interior of the crystal during the observations. The energetically most convenient disposition of these ions is that in which they are in the neighborhood of each other. In all these cases, we are therefore most likely to be dealing with a molecule consisting of positive and negative ions coupled by ionic bonding rather than the corresponding ions individually. Henceforth, we shall be concerned with gas crystals containing separated positive and negative ions. These ions are at the sites of the crystal lattice and this impedes their displacement.

We must now consider the essential features of the above system. If we drive alkali metal or halogen atoms into the gas crystal, it is often energetically more convenient to use positive ions of the alkali metals and negative ions of the halogens rather than neutral atoms. We note that this is not so in the case of the gaseous system because the electron affinity of any halogen atom is always less than the ionization potential of any alkali-metal atom. In the gas crystal, on the other hand, the polarization interaction between the ions and the ambient atoms will often modify this situation. We shall now consider this in some special cases.

Consider a gas crystal consisting of inert-gas atoms and containing alkali-metal ions. To determine the parameters of the system, we use the information on the two-body interaction potential between alkali-metal ions and inert-gas atoms. These data have been obtained by theoretical calculations⁹⁵⁻⁹⁸ and deduced from measurements of elastic ion-atom scattering cross sections^{99, 100} and of the mobility of the ions in the inert gas.¹⁰¹⁻¹⁰⁴ We shall base our discussion on the interaction potential between the alkali-metal ion and the inert-gas atom given by Mason and Schamp¹⁰¹

$$U_1(R) = -\frac{D}{2} \left[1.2 \left(\frac{r_m}{R} \right)^{12} - 0.8 \left(\frac{r_m}{R} \right)^9 - 2.4 \left(\frac{r_m}{R} \right)^4 \right]. \quad (10)$$

Table VIII lists the parameters of this potential for typical pairs, and also the following quantities determined from the formulas given above: $\delta\alpha$ —the difference be-

TABLE VIII. Interaction of alkali-metal ions with inert-gas atoms (two-body and in crystal lattice).

| System | K+ - Ar | Rb+ - Kr | Cs+ - Xe |
|-------------------------------|---------|----------|----------|
| D , eV | 0.42 | 0.42 | 0.44 |
| r_m , Å | 3.00 | 3.34 | 3.88 |
| $\delta\alpha$, Å | 0.35 | 0.20 | 0.12 |
| $(\hbar^2/MU_1^2)^{1/4}$, Å | 0.21 | 0.18 | 0.18 |
| $\Delta D/D_1$ | 0.009 | 0.006 | 0.006 |
| ΔU_{dist} , eV | 1.2 | 1.4 | 2.0 |
| ΔU , eV | 2.6 | 2.9 | 0.6 |
| $J - \Delta U$ | 1.7 | 1.3 | 0.6 |

tween the distance between two nearest atoms in the crystal and between the ion and the nearest atom, $(\hbar^2/MU_1^2)^{1/4}$ —a quantity of the order of the amplitude of the oscillation of the ion, and $\Delta D/D_1$ —relative change in the bonding energy of the ion and the nearest inert-gas atom in the crystal as compared with the bonding energy of these particles in the absence of the ambient atoms.

Comparison of Tables I and VIII will show that the interaction between the ion and the inert-gas atom is stronger as compared with the case of neutral particles. The implantation of the impurity ion will, therefore, produce substantial distortion of the gas-crystal lattice. Another feature of this system is that the interaction potential between the ion and the lattice contains an important contribution due to atoms that are not nearest neighbors. If we use the parameters of the face-centered lattice,³⁶ we find that

$$\Delta U_{\text{dist}} = \sum_i \frac{\alpha e^2}{2R_i^4} = \frac{13.1\alpha e^2}{2a^4}; \quad (11)$$

where α is the polarizability of the atom and the sum is evaluated over the atoms that are not the nearest neighbors of the ion, and a is the distance between two nearest lattice atoms. It is clear that ΔU_{dist} depends only on the lattice parameters and is independent of the type of ion. The total bonding energy of the ion to the crystal lattice is

$$\Delta U = \Delta U_{\text{dist}} + 12D_1, \quad (12)$$

where D_1 is the bonding energy between the ion and the nearest atom. Table VIII lists the values of ΔU_{dist} and ΔU for the systems under consideration. The quantity ΔU is comparable with the ionization potential J for the corresponding atom. Introduction of an alkali-metal atom into the inert-gas crystal will, as a rule, lead to a positive interaction energy between the atom and the lattice (the energy of the atom outside the lattice is taken to be zero). The two-body interaction potentials between the inert-gas atoms and the alkali-metal atoms are reasonably well known. They have been deduced from optical measurements,¹⁰⁴⁻¹⁰⁸ from scattering data,¹¹⁰⁻¹¹⁹ and from calculations.^{120, 121} The energies of interaction between alkali-metal atoms and inert-gas atoms in the crystal lattice are lower by an order of magnitude as compared with the energy of interaction for their ions. We shall, therefore, assume that the introduction of the alkali-metal ion into the lattice site of the inert-gas crystal leads to a change in the energy of the system as compared with the case when the cor-

responding alkali-metal atom is introduced. We shall represent this change by ΔU .

We now consider the case where the lattice sites of the inert-gas crystal contain both alkali-metal atoms and halogen atoms at a sufficient distance from each other. It then follows from Table VIII that the energetically most advantageous situation is where the system contains positive ions of the alkali metals and negative ions of the halogens. In fact, the binding energy of an electron to the negative ion¹²²⁻¹²⁶ is 3.40 eV for fluorine, 3.62 eV for chlorine, 3.37 eV for bromine, and 3.08 eV for iodine and, in each case, is appreciably greater than $J = \Delta U$. Moreover, the interaction potential between the negative ion of the halogen atom and the crystal lattice is of the same order and sign as for the positive ion of the alkali metal. It follows that, in this case, we have a frozen electrolyte which is stable with respect to the transition of the electron from the negative ion to the positive ion. Moreover, we shall suppose that this stability prevails during the formation of positive and negative ions of the alkali metal as well. In fact, the binding energy of an electron to the negative alkali-metal ion is¹²²⁻¹²⁶ approximately 0.5 eV and, if the negative alkali-metal ion and the nearest inert-gas atoms exhibit an attractive interaction, it follows from Table VIII that, in these particular cases, the presence of positive and negative alkali-metal ions is energetically more advantageous than the presence of the corresponding atoms. We note that this is valid so long as the separation between the neighboring impurity particles is large in comparison with the distance between the nearest atoms of the crystal. The system is unstable with respect to the formation of molecules from impurity particles, or of a separate phase, i.e., the crystal is metastable in this case.

Finally, we draw attention to one interesting feature of the frozen electrolyte. Since we are dealing with low temperatures and relatively high particle densities, we can easily produce a nonideal plasma in this case. Thus, in the case of the argon crystal at the boiling point of hydrogen ($T = 20.5$ K), the imperfection parameter $N_i e^6 / T^3$ is equal to unity for ion concentrations of 10^{-6} (N_i is the ion density and e is the electron charge). The nonideal plasma is thus more readily accessible in this case than in other physical situations.

Recombination between positive and negative ions in the inert-gas crystal lattice is different as compared with the situation where the impurity particles are atoms. In the present case, the ions approach one another under the influence of the electric field produced by them and the recombination coefficient between the positive and negative ions is given by the Langevin formula^{127, 122}

$$\alpha = 4\pi e (K_+ + K_-),$$

where K_+, K_- are the ion mobilities. If we use the Einstein relation¹²⁸ $K = eD/T$, where D is the diffusion coefficient, we obtain

$$\alpha = \frac{4\pi e^2 (D_+ + D_-)}{T}, \quad (13)$$

where D_+, D_- are the diffusion coefficients for the corresponding ions in the lattice. Hence, we find that the

characteristic lifetime of the system, i.e., the ion recombination time, is

$$\tau = \frac{1}{\alpha N_i} = \frac{\tau_0}{c_i}, \quad \tau_0 = \frac{T}{4\pi e^2 N_0 (D_+ + D_-)}, \quad (14)$$

where N_i is the ion density, $N_0 = \sqrt{2}/a^3$ is the density of atoms in the lattice, and $c_i = N_i/N_0$ is the concentration of ions in the lattice. It is clear that the dependence on the impurity concentration and on the diffusion coefficients in the expression for the lifetime of the metastable gas crystal containing impurity ions is the same as when the impurity particles are atoms.

Because the bonding energy of ions in the crystal lattice is high, their diffusion over the inert-gas lattice sites is even more retarded than in the case of the diffusion of impurity atoms. One would, therefore, expect that inert-gas crystals with imbedded ions will have relatively long lifetimes, just as in the case of crystals with impurity atoms. However, the polarization interaction between the ions and the crystal lattice produces substantial lattice distortions extending over a few atomic layers. This may give rise to new ion diffusion mechanisms, so that, in order to establish the prolonged existence of gas crystals with imbedded ions, one would have to perform additional experimental and theoretical studies of the diffusion of ions in gas crystals.

We note that our calculations of the parameters of particular gas crystals with imbedded particles have been confined to inert-gas crystals. This was dictated by the fact that the parameters of the interaction potentials between atoms can be calculated with a sufficient degree of reliability. It is clear that molecular crystals, and especially solid nitrogen, can also be used as a basis for the metastable gas crystals under investigation.

CONCLUSIONS

Studies involving atoms or radicals frozen into a gas-crystal matrix have demonstrated the value of such objects. They have established the parameters characterizing many of the radicals and have thrown light on the possible formation of bonding in exotic chemical compounds. They have also resulted in the production of compounds which could not be formed by other methods. However, our analysis has shown that, as a rule, the size of the imbedded particles in the experiments performed so far was different from the size of the atomic particles making up the gas crystal. This facilitates the displacement of the imbedded particles in the crystal and restricts the lifetime of such systems due to the recombination of atoms on radicals, or their participation in chemical reactions. The metastable gas crystal turns out to be more stable if the size of the impurity particle is close to the size of the crystal atoms, so that these particles get "stuck" at the sites of the crystal lattice. Such systems are practically stable and open up new possibilities for utilizing gas crystals with imbedded foreign atomic particles.

- ¹L. Andrews, *Ann. Rev. Phys. Chem.* **22**, 109 (1971).
- ²B. Meyer, *Low Temperature Spectroscopy*, Elsevier, N. Y., 1971.
- ³J. S. Ogden and J. J. Turner, *Chem. Brit.* **7**, 186 (1971).
- ⁴H. Hallam, *Vibrational Spectroscopy of Trapped Species*, Wiley, N. Y., 1972.
- ⁵A. J. Barnes, *Rev. Anal. Chem.* **1**, 193 (1972).
- ⁶G. C. Pimentel, *Angew. Chem.* **87**, 220 (1975); *Angew. Chem. Intern. Edit.* **14**, 199 (1975).
- ⁷D. A. Frank-Kamenetskiĭ, *Diffuziya i teploperedacha v khimicheskoĭ kinetike (Diffusion and Heat Transfer in Chemical Kinetics)*, Nauka, M., 1967.
- ⁸V. N. Kondrat'ev and E. E. Nikitin, *Kinetika i mekhanizm gazofaznykh reaktsii (Kinetics and the Mechanism of Reactions in the Gaseous Phase)*, Nauka, M., 1974, p. 451.
- ⁹B. M. Smirnov, *Asimptoticheskie metody v teorii atomnykh stolknovenii (Asymptotic Methods in the Theory of Atomic Collisions)*, Atomizdat, M., 1973.
- ¹⁰R. J. Munn, *J. Chem. Phys.* **40**, 1439 (1964).
- ¹¹R. Düren *et al.*, *Phys. Lett.* **18**, 282 (1965).
- ¹²R. J. Munn and F. J. Smith, *J. Chem. Phys.* **43**, 3998 (1965).
- ¹³L. Monchick *et al.*, *Phys. Rev. A* **139**, 1076 (1965).
- ¹⁴L. W. Bruch and I. J. McGee, *J. Chem. Phys.* **46**, 2959 (1967).
- ¹⁵D. E. Beck, *Mol. Phys.* **14**, 311 (1968).
- ¹⁶R. Helbig, W. Gaide, and H. Pauly, *Z. Phys.* **208**, 215 (1968).
- ¹⁷M. G. Dondi *et al.*, *J. Chem. Phys.* **51**, 392 (1969).
- ¹⁸L. W. Bruch and I. J. McGee, *J. Chem. Phys.* **52**, 5884 (1970).
- ¹⁹J. M. Parson *et al.*, *J. Chem. Phys.* **53**, 2123, 3755 (1970).
- ²⁰K. G. Anlauf, R. W. Bickes, and R. B. Bernstein, *J. Chem. Phys.* **54**, 3647 (1971).
- ²¹P. E. Siska *et al.*, *J. Chem. Phys.* **55**, 5762 (1971).
- ²²P. Cantini *et al.*, *J. Chem. Phys.* **56**, 1946 (1972).
- ²³J. M. Farrar and Y. T. Lee, *J. Chem. Phys.* **56**, 5801; **57**, 5492 (1972).
- ²⁴D. P. Morrow, J. P. Aldridge, and J. G. Skofronick, *J. Chem. Phys.* **59**, 2145 (1973).
- ²⁵J. M. Farrar *et al.*, *Chem. Phys. Lett.* **19**, 359 (1973).
- ²⁶C. Y. Ng, Y. T. Lee, and J. A. Barker, *J. Chem. Phys.* **61**, 1996 (1974).
- ²⁷U. Buck, *Adv. Chem. Phys.* **30**, 313 (1975).
- ²⁸R. W. Bickes *et al.*, *Farad. Disc. Chem. Soc.* **55**, 167 (1973).
- ²⁹V. Aquilanti *et al.*, *Chem. Phys. Lett.* **15**, 305 (1972).
- ³⁰P. Bassi *et al.*, *Phys. Rev. A* **13**, 584 (1976).
- ³¹V. Aquilanti *et al.*, *J. Chem. Phys.* **65**, 4751 (1976).
- ³²M. V. Smoluchowski, *Z. Phys. Chem.* **92**, 192 (1917).
- ³³J. J. Burton, *Phys. Rev.* **182**, 885 (1969).
- ³⁴H. R. Glyde and J. A. Venables, *J. Phys. Chem. Solids* **29**, 1093 (1968).
- ³⁵D. R. Squire and W. G. Hoover, *J. Chem. Phys.* **50**, 701 (1969).
- ³⁶J. O. Hirschfelder, C. P. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964. (Russ. transl. of an earlier edition, Fizmatgiz, M., 1962).
- ³⁷A. V. Chadwick and H. R. Glyde, in: *Rare Gas Solids*, ed. by M. L. Klein and J. A. Venables, Vol. 2, Ind., Academic Press, New York, 1977, p. 1151.
- ³⁸A. Berne, G. Boato, and N. de Baz, *Nuovo Cimento B* **46**, 182 (1966).
- ³⁹E. H. C. Parker, H. R. Glyde, and B. L. Smith, *Phys. Rev.* **176**, 1107 (1968).
- ⁴⁰A. V. Chadwick and J. A. Morrison, *Phys. Rev. B* **1**, 2748 (1970).
- ⁴¹R. Henry and R. E. Norberg, *Phys. Rev. B* **6**, 1642 (1972).
- ⁴²W. M. Yen and R. E. Norberg, *Phys. Rev.* **131**, 269 (1963).
- ⁴³B. N. Oscherin, *Phys. Status Solidi B* **43**, K59 (1971).
- ⁴⁴Van Witzenburg, *Phys. Lett. A* **25**, 293 (1967).
- ⁴⁵L. A. Schwable, *Phys. Rev. B* **14**, 1722 (1976).
- ⁴⁶B. L. Smith and J. A. Chapman, *Philos. Mag.* **15**, 739 (1967).
- ⁴⁷D. L. Losee and R. O. Simmons, *Phys. Rev.* **172**, 934 (1968).
- ⁴⁸E. P. Kündig, M. Moskovitz, and G. A. Ozin, *Can. J. Chem.* **50**, 3587 (1972).
- ⁴⁹A. Bos and A. T. Howe, *J. Chem. Soc. Farad. Trans.* **70**, 440, 451 (1974).
- ⁵⁰D. McIntosh, M. Moskovitz, and G. A. Ozin, *Inorg. Chem.* **15**, 1969 (1976).
- ⁵¹W. H. Childs, *Physical Constants*, 9th ed., Halsted, New York, 1973 (Russ. transl. of an earlier edition, Fizmatgiz, M., 1962).
- ⁵²J. Goodman and L. E. Brus, *J. Chem. Phys.* **65**, 3808 (1976).
- ⁵³G. Herzberg and A. Lagerqvist, *Can. J. Phys.* **46**, 2363 (1968).
- ⁵⁴L. J. Allamandola *et al.*, *J. Chem. Phys.* **67**, 99 (1977).
- ⁵⁵V. E. Bondybey and L. E. Brus, *J. Chem. Phys.* **63**, 786 (1975).
- ⁵⁶B. S. Ault and L. Andrews, *J. Chem. Phys.* **64**, 3075 (1976).
- ⁵⁷B. S. Ault and L. Andrews, *J. Chem. Phys.* **65**, 4192 (1976).
- ⁵⁸C. A. Brau and J. J. Ewing, *J. Chem. Phys.* **63**, 4640 (1975).
- ⁵⁹T. H. Dunning and P. J. Hay, *Appl. Phys. Lett.* **28**, 649 (1976).
- ⁶⁰D. McIntosh and G. A. Ozin, *J. Am. Chem. Soc.* **98**, 3167 (1976).
- ⁶¹D. McIntosh and G. A. Ozin, *Inorg. Chem.* **16**, 51 (1977).
- ⁶²F. J. Adrian and V. A. Bowers, *J. Chem. Phys.* **65**, 4316 (1976).
- ⁶³D. G. Cowgill and R. E. Norberg, *Phys. Rev. B* **13**, 2773 (1976).
- ⁶⁴V. E. Bondybey and L. E. Brus, *J. Chem. Phys.* **63**, 786, 794, 2223 (1975).
- ⁶⁵L. E. Brus and V. E. Bondybey, *J. Chem. Phys.* **63**, 3123 (1975).
- ⁶⁶V. E. Bondybey and G. Fletcher, *J. Chem. Phys.* **64**, 3615 (1976).
- ⁶⁷V. E. Bondybey and L. E. Brus, *J. Chem. Phys.* **64**, 3724 (1976).
- ⁶⁸L. E. Brus and V. E. Bondybey, *J. Chem. Phys.* **65**, 71 (1976).
- ⁶⁹J. Goodman and L. E. Brus, *J. Chem. Phys.* **65**, 1156 (1976).
- ⁷⁰V. E. Bondybey and G. C. Pimentel, *J. Chem. Phys.* **56**, 3832 (1972).
- ⁷¹L. Andrews, *J. Phys. Chem.* **73**, 3922 (1969).
- ⁷²R. R. Smardzewski and J. Andrews, *J. Phys. Chem.* **57**, 1327 (1972).
- ⁷³R. Spiker and L. Andrews, *J. Phys. Chem.* **58**, 713 (1973).
- ⁷⁴R. Spiker and L. Andrews, *J. Phys. Chem.* **58**, 702 (1973).
- ⁷⁵B. S. Ault and J. Andrews, *J. Phys. Chem.* **62**, 2312, 2320 (1975).
- ⁷⁶H. Huber, G. A. Ozin, and A. V. Voet, *Can. J. Chem.* **51**, 2722 (1973).
- ⁷⁷L. Andrews and R. R. Smardzewski, *J. Chem. Phys.* **58**, 2258 (1973).
- ⁷⁸H. Huber and G. A. Ozin, *J. Mol. Spectrosc.* **41**, 595 (1972).
- ⁷⁹L. Andrews, J. T. Hwang, and C. Trindle, *J. Phys. Chem.* **77**, 1065 (1973).
- ⁸⁰L. Andrews, *J. Phys. Chem.* **50**, 4288 (1969).
- ⁸¹L. Andrews, *J. Phys. Chem.* **54**, 4935 (1971).
- ⁸²J. H. Darling, M. B. Garton-Sprenger, and J. S. Ogden, *J. Chem. Soc. Farad. Trans.* **2**, 75 (1973).
- ⁸³D. McIntosh and G. A. Ozin, *Inorg. Chem.* **15**, 2869 (1976).
- ⁸⁴R. C. Spiker and L. Andrews, *J. Chem. Phys.* **59**, 1851, 1863 (1973).
- ⁸⁵H. Huber *et al.*, *J. Am. Chem. Soc.* **97**, 2097 (1975).
- ⁸⁶R. K. DeKock, *Inorg. Chem.* **10**, 1205 (1971).
- ⁸⁷J. L. Slater *et al.*, *J. Chem. Phys.* **55**, 5129 (1971).
- ⁸⁸H. Huber *et al.*, *J. Am. Chem. Soc.* **95**, 332 (1973).
- ⁸⁹M. Moskovitz and G. A. Ozin, *J. Chem. Phys.* **58**, 1251 (1973).
- ⁹⁰G. A. Ozin *et al.*, *Can. J. Chem.* **50**, 2385 (1972).
- ⁹¹D. W. Green and G. T. Reedy, *J. Chem. Phys.* **65**, 2921 (1976).
- ⁹²L. Andrews and J. I. Raymond, *J. Chem. Phys.* **55**, 3078 (1971).
- ⁹³D. W. Green, S. D. Gabelnick, and G. T. Reedy, *J. Chem. Phys.* **64**, 1697 (1976).
- ⁹⁴G. Ritzhaupt and J. P. Devlin, *J. Phys. Chem.* **81**, 521 (1977).
- ⁹⁵M. G. Menendez, M. J. Redmon, and J. F. Aebischer, *Phys. Rev.* **180**, 69 (1969).
- ⁹⁶L. Ya. Efrementkova, A. A. Radsig, and B. M. Smirnov, *Opt.*

- Spektrosk. **36**, 61 (1974) [Opt. Spectrosc. (USSR) **36**, 35 (1974)].
- ⁹⁷Y. S. Kim and R. G. Gordon, J. Chem. Phys. **61**, 1 (1974).
- ⁹⁸F. A. Gianturco, J. Chem. Phys. **64**, 1973 (1976).
- ⁹⁹T. R. Powers and R. J. Cross, J. Chem. Phys. **58**, 626 (1973).
- ¹⁰⁰F. E. Budenholzer, E. A. Gislason, and A. D. Jorgensen, J. Chem. Phys. **66**, 4832 (1977).
- ¹⁰¹A. Mason and H. W. Schamp, Ann. Phys. (N. Y.) **4**, 233 (1958).
- ¹⁰²H. R. Skullerud, J. Phys. B **6**, 918 (1973).
- ¹⁰³R. P. Creaser, J. Phys. B **7**, 529 (1974).
- ¹⁰⁴M. Riggin, Can. J. Phys. **52**, 1683 (1974).
- ¹⁰⁵R. E. M. Hedges, D. L. Drummond, and A. Gallagher, Phys. Rev. A **6**, 1519 (1972).
- ¹⁰⁶D. L. Drummond and A. Gallagher, J. Chem. Phys. **60**, 3426 (1974).
- ¹⁰⁷C. G. Carrington and A. Gallagher, J. Chem. Phys. **60**, 3436 (1974).
- ¹⁰⁸G. York, R. Scherps, and A. Gallagher, J. Chem. Phys. **63**, 1052 (1975).
- ¹⁰⁹R. E. Smalley *et al.* J. Chem. Phys. **66**, 3778 (1976).
- ¹¹⁰D. E. Beck and H. J. Liesch, Z. Phys. **195**, 444 (1966).
- ¹¹¹U. Buck and H. Pauly, Z. Phys. **208**, 390 (1968).
- ¹¹²R. Düren, G. P. Raabe, and C. Schlier, Z. Phys. **214**, 410 (1968).
- ¹¹³H. G. Bennewitz, R. Haerten, and G. Müller, Z. Phys. **226**, 139 (1969).
- ¹¹⁴C. J. Malerich and R. J. Cross, J. Chem. Phys. **52**, 386 (1970).
- ¹¹⁵J. G. R. Okel and Van De Ree, J. Chem. Phys. **54**, 4259 (1971).
- ¹¹⁶G. B. Ury and L. Wharton, J. Chem. Phys. **56**, 5832 (1972).
- ¹¹⁷P. Dehmer and L. Wharton, J. Chem. Phys. **57**, 4821 (1972).
- ¹¹⁸C. J. Malerich, K. B. Povodator, and R. J. Cross, Chem. Phys. **20**, 409 (1977).
- ¹¹⁹T. Kneser *et al.*, J. Phys. B **10**, 2407 (1977).
- ¹²⁰W. E. Baylis, J. Chem. Phys. **51**, 2665 (1969).
- ¹²¹J. Pascale and J. Vanderlanque, J. Chem. Phys. **60**, 2278 (1974).
- ¹²²B. M. Smirnov, Iony i vzbuzhdennye atomy v plazme (Ions and Excited Atoms in Plasmas), Atomizdat, M., 1974.
- ¹²³H. Hotop and W. C. Lineberger, J. Phys. Chem. Ref. Data **4**, 539 (1975).
- ¹²⁴H. S. W. Massey, Negative Ions, Cambridge University Press, 1976.
- ¹²⁵B. L. Moiseiwitsch, in: Atomic Processes and Applications, ed. by P. C. Burke and B. L. Moiseiwitsch, North-Holland, Amsterdam, 1976, p. 291.
- ¹²⁶B. M. Smirnov, Otritsatel'nye iony (Negative Ions), Atomizdat, M., 1978.
- ¹²⁷P. Langevin, Ann. Chem. Phys. (Paris) **8**, 245 (1905).
- ¹²⁸L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred (Fluid Mechanics), Gostekhizdat, M., 1954 (English Transl., Pergamon Press, Oxford).

Translated by S. Chomet