precise, expanding the function $\nu(\theta)$ in Legendre polynomials, we equate the coefficients for the same polynomials. Limiting ourselves to two, three and four harmonics, we obtain the results (25), (28) and (29), respectively. But the role of the conserved quantities would not be revealed in such a method of solutions.

4)The times $t_{\parallel}$ calculated for "strong" anomalous dispersion dispersion[3] and weak dispersion[18] differ only by a numerical factor ~2.

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[1] B. Esel'son, M. Kaganov, É. Rudavskiĭ, and I. Serbin, Usp. Fiz. Nauk **112**, 591 (1974) [Sov. Phys. Usp. **17**, 215 (1974)].
[2] H. Maris and W. Massey, Phys. Rev. Lett. **25**, 220 (1970).
[3] H. Maris, Phys. Rev. **A8**, 1980, 2639 (1973); **A9**, 1412 (1963).
[4] D. Benin, Phys. Rev. **B11**, 145 (1975).
[5] V. Gurevich and B. Laĭkhtman, Zh. Eksp. Teor. Fiz. **69**, 1230 (1975) [Sov. Phys. JETP **42**, 628 (1975)].
[6] I. Khalatnikov and D. Chernikova, Zh. Eksp. Teor. Fiz. **49**, 1957 (1965); **50**, 4116 (1966) [Sov. Phys. JETP **22**, 1336 (1966); **23**, 274 (1966)].
[7] R. Wehner, Phys. Rev. **A9**, 2625 (1974).
[8] N. G. Mills, R. A. Sherlock, and A. Wyatt, Phys. Rev. Lett. **32**, 978 (1974); W. Junker and C. Elbaum, Phys. Lett. **57A**, 432 (1976).
[9] Yu. Matveev and I. Khalatnikov, Pis'ma Zh. Eksp. Teor. Fiz. **22**, 581 (1975) [JETP Lett. **22**, 285 (1975)].
[10] J. Jäckle and K. Kehr, Phys. Rev. **A9**, 1757 (1974).
[11] L. Landau and I. Khalatnikov, Zh. Eksp. Teor. Fiz. **19**, 637, 709 (1949).
[12] I. Khalatnikov, Teoriya sverkhtekuchësti (Theory of Superfluidity) Nauka, 1971.
[13] I. Gradshteĭn and I. Ryzhik, Tablitsy integralov, summ. radov i proizvedenic (Tables of Integrals, Sums, Series, and Products), Nauka, 1971.
[14] V. Gurevich and B. Laĭkhtman, Zh. Eksp. Teor. Fiz. **70**, 1907 (1976) [Sov. Phys. JETP **43**, 993 (1976)].
[15] D. Benin, Phys. Rev. **B13**, 1105 (1976).
[16] H. Jeffreys and B. S. Jeffreys, Methods of Mathematical Physics, Cambridge Univ. Press, 1956, v. 3.
[17] C. Carroll, Phys. Rev. **A2**, 497 (1970).
[18] R. Wehner and R. Klein, Phys. Rev. Lett. **23**, 1372 (1969).
[19] A. Woods and R. Cowley, Rep. Progr. Phys. **36**, 1135 (1973).
[20] O. Dietrich, E. Graf, C. Huang, and L. Russel, Phys. Rev. **A5**, 1377 (1972).

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Thermal stability of condensed systems that contain trapped atoms

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A consistent analysis of the thermal stability of atom-containing condensed systems, based on recently obtained experimental data, shows that, notwithstanding the previous opinion expressed in the literature, that when the temperature of the experiment is lowered one should expect an appreciable increase of the concentration of the trapped atoms. The analysis shows that to trap atoms in a solid matrix by means of a magnetic field the field intensity required is quite large and exceeds by several orders the fields at which $\mu_e B/k_B T \approx 1$. In addition, a magnetic field can be effectively used for trapping only if there is no contact between the atoms prior to the establishment of equilibrium between them and the magnetic field. The use of beams polarized in advance does not facilitate the problem to any extent.

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Recent progress in cryogenics and in the technique of obtaining strong magnetic fields have increased in the stabilization of appreciable concentrations of atoms in solid matrices at low temperatures. The most attractive in this respect are metstable (with high energy content) mixtures, both from the point of view of their use as rocket fuel[1,2] and in connection with the possiblity of producing metallic superconducting phases (metallic hydrogen and nitrogen[3]) and superfluid phases (triplet hydrogen[4]). In his review[5] devoted to prospects of progress in science, Ginzburg included the problem of obtaining these phases among the most interesting and important tasks of modern physics.

The necessary condition for the existence of metastable systems containing atoms whose stable states are molecules is that recombination of the atoms be kinetically hindered. The cause of the kinetic hindrances may be either the existence of an energy barrier to the motion of the atoms over the matrix (activated diffusion), or the presence of an activation energy in the recombination act itself, because of the interaction of the atoms with the matrix and with one another, or because of alignment of their electron spins in strong magnetic fields.1)

However, in view of the large energy reserves in systems that contain appreciable numbers of "quasi-free" atoms, slowness of the isothermal decay of the system in comparison with the observation time is far from a sufficient condition of the system stability. The reason lies in the thermal explosion of chemically active gas mixtures.[6]

It is precisely thermal instability that was used to explain the experiment results of the 50's and 60's, namely the obtained small concentrations of the atoms and free radicals at low temperatures (relative atom content $\lesssim 0.1\%$) when frozen out of an electric discharge on cold surfaces, or when produced by radiation chemistry in a solid matrix at low temperatures.[1] It was assumed that the atoms (or the free radicals) become stabilized in structure traps of the matrix, and the thermal instability was attributed to "unfreezing" of their diffusion upon passage of the thermal wave from the center of the random recombination.[7,8] This led to weak dependences of the limiting atom concentrations n_{cr} on the matrix temperature T_0 and on the depths E of the structure traps ($E/k_B \gg T_0$, where k_B is Boltzmann's constant):

$$n_{cr} \sim \left(\frac{E}{k_B} - T_0\right)^{1/2} \text{ [7] or}$$

$$n_{cr} \sim \alpha \frac{E}{k_B} - T_0 \text{ [8]}.$$

The most important shortcoming of this approach, besides its being based on a simplified model, is the lack of an analysis of the stability of samples having finite dimensions and containing atoms in the traps, with respect to the ordinary thermal explosion that occurs when the thermal conductivity cannot dissipat all the heat released in the "dark" chemical reaction.[9] While yielding, for a certain choice of parameters, values close to those observed in experiment, the theories mentioned above[7,8] were unable to explain why the experimental concentration of the hydrogen atoms is smaller by more than three orders (and not by several times, as would follow from a comparison of the polarizabilities) than the number of nitrogen atoms. In addition, the important conclusion that it is not useful to decrease the sample temperature below 5–10 K in order to increase n_{cr} substantially could not be verified within the capabilities of the then-existing experimental procedures, because the medium became strongly overheated upon precipitation or radiation, and because the temperature of the condensed gas was high.

Our recent experiments[10,11] performed by a new procedure[12] based on introducing an atomic beam into superfluid helium through its surface, have shown that if the heat removal is good and the temperature is low ($T_0 \approx 1.5$ K), then the concentrations of the stabilized nitrogen atoms are higher by at least one order of magnitude than those previously attained. It turned out, in addition, that an appreciable fraction of the nitrogen atoms accumulated at $T_0 < 2$ K recombine explosively when heated at the λ point ($T_\lambda \approx 2.19$ K) (see Fig. 1). Since only the thermal conductivity of liquid helium changes jumpwise at the λ point, it was natural to connect this effect with thermal explosion of granules suspended in the liquid and containing nitrogen atoms.[10] These circumstances made it necessary to re-examine the thermal stability of condensed systems that contain atoms in structure traps. In addition, we consider in the present paper the stabilization of similar systems by a constant magnetic field.

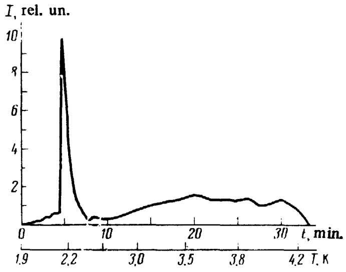

FIG. 1. Dependence of the luminescence intensity ($\lambda \sim 523$ nm) of a condensate containing nitrogen atoms on the helium temperature.

I. THEORETICAL MODELS

A. Stabilization of atoms in structure traps

Assume for simplicity that all the traps have identical depths E and that their number is close to the number M of the molecules. Then the thermal processes of ejection of an atom from a trap, and its capture, can be written in the form

$$AM \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A+M, \tag{I}$$

where $k_1 = k_1^0 \exp(-E/k_B T)$ and $k_{-1} = k_{-1}^0$ (the reverse processes are assumed not to be activated). Recombination is possible both between free atoms:

$$A+A \xrightarrow{k_2^0} A_2+D, \tag{II}$$

and between a free and bound atom:

$$A+AM \xrightarrow{k_2} A_2+M+D \tag{II'}$$

(the dissociation energy $D \gg E$).

For the relative concentration of the atoms in the matrix

$$n \equiv \frac{[AM]+[A]}{[M]}$$

we can easily obtain the kinetic equation

$$\frac{dn}{dt} = -2\left\{ k_2 n + (k_2^0 - k_2)\frac{[A]}{[M]}\right\}[A]. \tag{1}$$

If the structure traps are responsible for the stabilization, then $[A] \ll [AM]$. From the condition that the system be quasistationary with respect to the concentration of the free atoms, it follows that

$$[A] = k_1 n/(k_{-1} + k_2 n). \tag{2}$$

Recognizing that k_{-1} and k_2 are of the same order (and are close to the gas-kinetic rate constants), and that $n \ll 1$, we obtain from (1) and (2)

$$W_{\text{chem}} \equiv -\frac{dn}{dt} = 2\frac{k_2 k_1}{k_{-1}} n^2 \approx 2 k_1^0 n^2 \exp\left(-\frac{E}{k_B T}\right) \tag{3}$$

(k_1^0 is close to the lattice-vibration frequency, $k_1^0 = 10^{12} - 10^{14}$ sec^{-1}). The corresponding rate of heat release is

$$q = DW_{\text{chem}} \approx k_1 D n^2 \exp(-E/k_B T). \tag{4}$$

B. Trapping atoms by orienting the electron spins

The possibility of preventing recombination of paramagnetic atoms by aligning their electron spins in a constant magnetic field is due with the need, if a chemical bond is to be formed and the dissociation energy released, for "pairing" electrons with oppositely directed spin. On the other hand, the triplet interaction curve (for atoms with $S=1/2$) is repulsive at distances $r<4\,\text{Å}$, and the presence of a shallow potential well at $r\approx 4\,\text{Å}$ gives grounds for hoping to stabilize the triplet phase.[4] It follows therefore that in first-order approximation the magnetic field B, at an equilibrium population of the magnetic sublevels, should lead to the onset of an energy barrier to recombination, equal to the splitting of the levels in the field. Its influence can be taken into account by replacing E in (4) by $E+4\mu_e SB$ (μ_e is the electron Bohr magneton and S is the spin).[13] 2)

II. THERMAL STABILITY OF SYSTEM

The heat-conduction equation of a medium with a heat source is of the form

$$c\rho\,\partial T/\partial t=\varkappa\Delta T+q(\mathbf{r},t), \tag{5}$$

where c, ρ, and $\varkappa$ are the specific heat, the density, and thermal conductivity of the matrix, while $q(\mathbf{r},t)$ is the heat released at the point $\mathbf{r}$ at the instant of time t, and is given by expression (4):

$$q=q_0(\mathbf{r},t)\exp(-E_{\text{eff}}/k_BT).$$

It is convenient to consider two physically different regimes in which thermal instability sets in.

1. *Nonstationary thermal wave in an infinite medium*. In this case the stability condition means that the thermal wave traveling from the center of random recombination does not manage to unduce thermally, during its lifetime, recombination of neighboring atoms in the matrix. The lack of stability can be called thermal explosion. 3)

2. *Stationary heat removal through the boundaries of the medium.* The stability condition requires that the rate of removal of the heat of recombination by such as to ensure a stationary temperature of the medium. This case is perfectly analogous, physically and its mathematical description, to thermal explosion of mixtures of gases that can react chemically.[15,16]

A. Thermal-wave explosion

Consider a thermal wave propagating from the center ($r=0$, $t=0$) of a random recombination. If c, ρ, and λ are independent of temperature, the wave equation takes the form[17]

$$T(r,t)-T_0=\frac{D}{c\rho(4\pi\lambda t)^{3/2}}\exp\left(-\frac{r^2}{4\lambda t}\right), \tag{6}$$

where $\lambda=\varkappa/\rho c$ is the thermal diffusivity of the medium.

Heat transfer in a condensed matrix with powerful "pointlike" energy-release sources is a rather complicated process. An analysis based on the macroscopic heat-conduction equation must therefore be regarded only as a source of simple qualitative estimates that explain the character and the scale of the effect.

The condition that the system be stable to the passage of a thermal wave is written, with (3) taken into account, in the form:

$$\int_{0}^{\infty}\int_{0}^{\infty}[M]W_{\text{chem}}\cdot 4\pi r^2 dr\,dt=k_{\text{eff}}[M]n^2\int_r\int_t\exp\left(-\frac{E_{\text{eff}}}{k_BT}\right)4\pi r^2dr\,dt\leqslant 1. \tag{7}$$

where k_{eff} is the coefficient of the exponential in the expression (3) for W_{chem}. Introducing the notation

$$\frac{Dk_B}{E_{\text{eff}}\rho c\pi^{3/2}}=a^3,\quad \frac{k_BT_0}{E_{\text{eff}}}=\gamma_0$$

and changing over to new variables $\tau=4\lambda t/r^2$ and $\xi=r/a$, we rewrite the integral in (7) in the form

$$J=\frac{\pi a^5}{\lambda}\int_\xi\int_\tau\xi^4\exp\left(-\frac{1}{\gamma_0+\xi^{-3}\tau^{-3/2}\exp(-\tau^{-1})}\right)d\xi\,d\tau.$$

The asymptotic value of J is[18]

$$J\approx 0.2\frac{a^5}{\lambda}\left(1+\frac{20}{9}\gamma_0\right). \tag{8}$$

From (7) and (8) we get a criterion for the stability of the system to a thermal-wave explosion:

$$n\leqslant n_{\text{cr}}\approx 9.4\left(\frac{\lambda}{k_{\text{eff}}[M]}\right)^{1/2}\left(\frac{E_{\text{eff}}\rho c}{Dk_B}\right)^{5/6}\left(1-\frac{10}{9}\frac{k_BT}{E_{\text{eff}}}\right). \tag{9}$$

This expression for n_{cr} differs noticeably from the analogous expressions obtained in[7] and[8]. The reason can be easily discerned by a qualitative consideration of the stability (criterion (7)) if the temperature dependence of the speed of the departure of the atom from the trap is replaced by a "step function": $k_1=k_1^0$ for $T\geqslant T^*$ $\equiv E_{\text{eff}}\,k_B$ and $k=0$ for $T<T^*$. The criterion (7) then takes the form

$$k_1{}^0n^2r_*{}^3t_*[M]\xi\leqslant 1, \tag{10}$$

where $r_*=[D/c\rho\pi^{3/2}(T^*-T_0)]^{1/3}$ is the distance over which a temperature higher than T^* is realized, t_x $=r_*^2/4\lambda$ is the duration of the overheating $T>T^*$ at the random-recombination center, and ξ is a numerical factor. The assumption that the atom leaves the trap immediately as the critical temperature T^* is reached ($T^*\gg T_0$) regardless of the duration of the overheating[7] is equivalent to omitting the time factor t_* from (10). As a result $n_{\text{cr}}\sim r^{-3/2}\sim\sqrt{T^*-T_0}$ and is not a function of the parameter that determines the time dependence of the cooling of the medium, i.e., of the thermal diffusivity λ.

In[8] the wave was simulated, without physical justification, by a rectangular pulse of constant amplitude, normalized to the energy. This approximation should

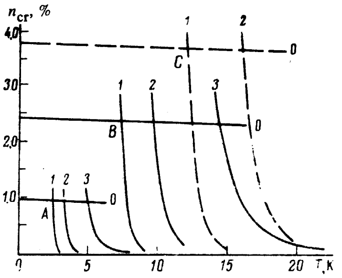

FIG. 2. Temperature dependence of limiting concentration of nitrogen atoms, calculated for the thermal-wave mechanism (0) and the thermal mechanism ($1-r_0=1$ cm, $2-r_0=10^{-2}$ cm, $3-r_0=10^{-4}$ cm) of the explosions. A) $E_{act}=200$ cal/mole; B) $E_{act}=600$ cal/mole; C) $E_{act}=1000$ cal/mole (for $\alpha=9\times10^{-11}$ cm/deg$^{1/2}$ and $\beta=2.5$ deg$^{-1/3}$cm^{-1}).

undervalue n_{cr}, since the overestimate of the exponential factor ($\exp\{-E/k_B[T_0+T(r,t)]\}$) turns out to prevail over the corresponding underestimate of the wave duration.4)

Figure 2 shows plots of $n_{cr}(T_0)$ for nitrogen atoms at E_{eff} equal to 200, 600, and 1000 cal/mole (the choice of this values of E_{eff} was based on the data of[8,20,21]).

B. Thermal explosion

According to[9], the explosion of the sample should take place when the heat rise of its interior relative to the boundary temperature is given by $\Delta T=k_BT_0^2\gamma/D$ ($\gamma\approx1$). The critical linear dimension of the sample, above which explosion takes place, is given by

$$r_{cr}=\left(\frac{\delta\varkappa k_BT_0{}^2}{DE_{eff}W_{chem}(T_0)}\right)^{1/2}, \tag{11}$$

where $\delta\approx1$. Substituting $W_{chem}(T_0)$ from (3) in (11), we express the critical atom concentration in the sample in terms of its linear dimension:

$$n_{cr}=\left[\frac{\delta\varkappa k_BT^2}{E_{eff}k_{eff}D[M]r_0{}^2\exp(E_{eff}/k_BT)}\right]^{1/2}. \tag{12}$$

Figure 2 shows plots of $n_{cr}(T_0)$ calculated for nitrogen on the basis of formula (12) for r_0 values 10^{-4}, 10^{-2}, and 1 cm, and for E_{eff} equal to 200, 600, and 1000 cal/mole.

C. Limiting atom concentrations

Thus, an analysis of the thermal stability of systems containing stabilized atoms leads to the following expression for the critical relative concentration of the atoms:

$$n_{cr}=\alpha\cdot\min\left\{\begin{array}{l}\dfrac{T}{r_0}\left[\dfrac{\exp[T^*/T]}{T^*}\right]^{1/2}\\ \beta(T^*)^{5/6}\left(1-\dfrac{10}{9}\dfrac{T}{T^*}\right)\end{array}\right., \tag{13}$$

where

$$\alpha=(\delta\lambda c\rho/k_{eff}[M]D)^{1/2},\ \beta=5.2(c\rho/D)^{1/3},\ T^*=E_{eff}/k_B.$$

The limiting concentrations of atoms stabilized at very low temperatures are determined by the stability of the system to thermal-wave explosion. At higher temperatures, stability to thermal explosion is decisive. In this region, in contrast to that of low temperatures, the limiting concentration depends very strongly (exponentially) on the temperature. As seen from Fig. 2, at reasonable values of the matrix parameters E_{eff}, $\varkappa$, c, and ρ, even for samples with small dimensions ($r\approx10^{-2}$ cm), the transition region is at ~4 K and below. When atoms settle on a cold substrate or condense in a liquid, during the initial stages the maximal values of n_{cr} are determined by the stability to thermal-wave explosion: regardless of the concentration of the atoms in the gas phase, their concentration in the matrix cannot exceed the limiting value and depends little on the substrate temperature T_0. At constant T_0, further accumulation of the condensate leads ultimately to internal superheating, and hence to thermal explosion. As a result, the atom concentration decreases sharply to very low values, or else at sufficiently large values of n explosive sulbimation of the condensate takes place (as it did in our experiments[10]). In fact, Fontana,[22,23] freezing nitrogen atoms on a glass substrate cooled to 4.2 K, observed at first a linear growth of the number of trapped atoms with precipation time, but when the sample thickness reached ~10^{-3} cm the number of atoms decreased sharply, by at less one order of magnitude.

Thermal explosion can occur also if the thermophysical properties of the medium are abruptly changed. Thus, for example, if the atoms are condensed, as in[10], in superfluid helium, the passage through the λ point in the course of heating causes a jumplike change of the thermal-conductivity coefficient, the condensate particles in the HeI become thermally insulated, and explosive recombination of the atoms takes place (see Fig. 1). Similar effects resulted (see[10]) also from vanishing of a film of superfluid helium from condensate deposited on the glass walls of the vesse above the surface of HeII. All this indicates that even at 1.5 – 2.0 K the concentration of the stabilized nitrogen atoms is limited by the thermal explosion and therefore, the opinion accepted in the literature notwithstanding, lowering the temperature below 4 K should lead to a substantial increase of this concentration. This is experimentally confirmed by the very fact that very large nitrogen-atom concentrations ($[N]/[N_2]>1.6\%$ have been obtained when the atoms were precipitated in superfluid helium ($T\approx1.5$ K).[10]

The foregoing is all the more true for hydrogen atoms: in view of their lower polarizability, and hence the smaller value of E_{eff}, the transition to the region controlled by the thermal-wave explosion should occur at noticeably lower temperatures. This conclusion agrees well with the fact that in our experiments[19] (as well as in earlier studies[1]) the hydrogen-atom concentration, under similar conditions, was incomparably smaller than that of nitrogen.

D. Stabilization of atoms by a magnetic field

Figure 3, which shows plots of $n_{cr}(B)$ obtained from the condition that the nitrogen atoms be stable to sta-

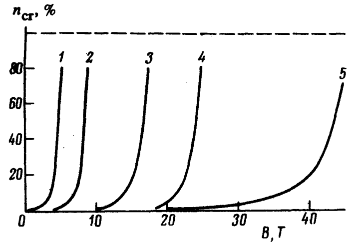

FIG. 3. Limiting concentration of nitrogen atoms vs magnetic field, as calculated from formula (12):

tionary thermal explosion, for the case of strong magnetic fields, when the alignment of the spins is the main obstacle to recombination ($\rho \approx 0.04$ mole/cm^3, $\lambda = 10^{-3}$ cm^3/sec, $c = 1$ cal/mole-deg, and $r = 10^{-4}$, cm) gives an idea of the scale of the fields needed for stabilizations. These fields are very strong: For $[N] \approx 5$ mol.% and $T_0 = 1$ K (curve 1, the critical field is $B = 20$ T, i.e., $\mu_e B/k_B T \approx 30$, and the transition to an effective stabilizing influence of the field is very abrupt, following a 15–20 percent increase of the field. The energy obstacles in the very act of recombination, for example those due to the interaction of the atoms with the matrix or with one another, can lead to a certain lowering of the fields needed for the stabilization. However, as seen from Fig. 3 (curves 1–3, $E_{act} = 20$ cal/mole), the scale of the critical fields is not significantly changed thereby.

We note that, just as for stabilization of atoms by structure traps, the simple analysis presented here is valid only at small n_{cr} ($\lesssim 1\%$). At larger concentrations (under conditions when they can be realized), it is necessary to take into account the change of the thermophysical characteristics, the spin-spin interactions, and the possible phase separation.

The large values of B needed to trap noticeable concentrations of atoms are in themselves a source of doubts concerning the advisability of using magnetic fields. But it must also be taken into account that the presented estimates are valid only for a spin system that is in complete equilibrium with the magnetic field, when $\eta = n_\uparrow/(n_\uparrow + n_\downarrow) \approx \exp(-2\mu_e B/k_B T) \approx 10^{-3}$ (for atoms with $S = 1/2$), where $n_\uparrow$ and $n_\downarrow$ are the populations of the upper and lower sublevels. In view of the relative slowness of the spin-lattice relaxation at low temperatures, so high a degree of atom polarization is reached far from instantaneously. Taking into account the possible initial (prior to condensation beam polarization η_0, the time τ_{in} needed to reach a polarization η close to the equilibrium value $\langle\eta\rangle$ ($\eta - \langle\eta\rangle \sim \langle\eta\rangle$ amounts to (neglecting the dependence of the time T_{SL} of the spin lattice relaxation on B)

$$\tau_{in} \approx T_{SL}\left(\frac{2\mu_e B}{k_B T} + \ln \eta_0\right). \tag{14}$$

This time is several tenfold the value of T_{SL} and decreases insignificantly when the initial spin polarization of the atom beam is used, since the technically attainable value is $\eta_0^{-1} \leqslant 10^4$.

TABLE I.

Curve No.	E_{act}, cal/mole	r_0, cm	T, K
1	20	10^{-4}	0.5
2	20	10^{-2}	[illegible]
3	20	10^{-4}	1.0
4	0	10^{-4}	1.0
5	200	10^{-3}	4.0

In our opinion, it is advisable to use magnetic field only for auxiliary purposes, to decrease the recombination probability during the initial stages of the atom-beam condensation, before the atoms have become stabilized via the principal mechanism (by traps or by formation of a new phase). It is possible to use for this purpose also preliminary polarization of the beam.

The authors thank Yu. L. Moskvin for useful discussions.

[1)] Interest in the problem of low-temperature trapping of paramagnetic atoms in strong magnetic fields has increased recently, and accumulation of large (~10%) concentrations of hydrogen atoms at $H = 5$T and $T = 2$K has been reported.[2]

[2)] Even very strong magnetic fields are insufficient to orient the nuclear magnetic moments (if they exist at all), so that the interaction of the nuclear and electronic moments can increase noticeably the recombination probability at $\mu_e B/k_B T \ll 1$.[14] The probability of the change of the total electric spin may even be more strongly influenced by its interaction with the orbital momentum of the system.

[3)] The term "thermal chain explosion" introduced in[8] seems less appropriate to us.

[4)] The recombination model used in[8] is also somewhat far-fetched (see[19]).

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[1] Formation and Trapping of Free Radicals, A. M. Bass and H. P. Broida, eds., Academic, 1960 [Russ. Transl., IIL, 1962].

[2] G. Rosen, AIAA Journal 12, 1325 (1974).

[3] E. G. Brovman, Yu. Kagan, and A. Kholas, Zh. Eksp. Teor. Fiz. **61**, 2429 (1971) [Sov. Phys. JETP **34**, 1300 (1972)]; E. G. Brovman, Yu. Kagan, A. Kholas, and V. V. Pushkarev, Pis'ma Zh. Eksp. Teor. Fiz. 18, 269 (1973) [JETP Lett. 18, 160 (1973)].

[4] R. D. Etters, J. V. Dugan, and R. W. Palmer, J. Chem. Phys. **62**, 313 (1975).

[5] V. L. Ginzburg, Usp. Fiz. Nauk **103**, 87 (1971) [Sov. Phys. Usp. **14**, 21 (1971)].

[6] N. N. Semenov, O nekotorykh problemakh khimicheskoĭ kinetiki i reaktsionnoĭ sposobnosti (Some Problems of Chemical Kinetics and Reactivity), Akad. Nauk SSSR, 1958.

[7] J. L. Jackson, J. Chem. Phys. **30**, 154 (1959).

[8] G. K. Vasil'ev and V. L. Tal'roze, Kinet. Katal. IV, 497 (1963).

[9] D. A. Frank-Kamenetskiĭ, Diffuziya i teploperedacha v khimicheskoi kinetike (Diffusion and Heat Transfer in Chemical Kinetics), Gostekhizdat, 1947.

[10] E. B. Gordon, L. P. Mezhov-Deglin, and O. F. Pugachev, Pis'ma Zh. Eksp. Teor. Fiz. **19**, 103 (1974) [JETP Lett. **19**, 63 (1974)].

[11] E. B. Gordon, L. P. Mezhov-Deglin, O. F. Pugachev, and V. V. Khmelenko, Abstracts of Papers Nineteenth All-Union Conf. on Low Temp. Physics, Minsk, 1976, p. 76.

[12] G. B. Gordon, L. P. Mezhov-Deglin, O. F. Pugachev, and V. V. Khmelenko, Prib. Tekh. Eksp. **6**, 247 (1975).

[13] V. S. Letokhov and Yu. E. Lozovik, Pis'ma Zh. Tekh. Fiz. **1**, 609 (1975) [Sov. Tech. Phys. Lett. **1**, 272 (1975)].

[14]M. Windsor, Trapped Radicals in Reaction Technology, see[1] (p. 446 of Russ. transl.).

[15]Ya. B. Zel'dovich, Zh. Eksp. Teor. Fiz. 9, 1530 (1939).

[16]D. A. Frank-Kamenetskiĭ, Zh. Fiz. Khim 13, 738 (1939).

[17]V. I. Smirnov, Kurs vyssheĭ matematiki (Course of Higher Mathematics), 2, Fizmatgiz, 1961.

[18]A. B. Migdal and V. P. Kraĭnov, Priblizhennye metody kvantovoĭ mekhaniki (Approximate Methods of Quantum Mechanics), Nauka, 1966.

[19]O. F. Pugachev, Candidates's Dissertation, Moscow Phys. Tech. Inst., 1975.

[20]B. Brocklehurst and J. L. Pimentel, J. Chem. Phys. **36**, 2040 (1962).

[21]A. L. Berlad, J. Chem. Phys. **35**, 1180 (1961).

[22]B. J. Fontana, J. Appl. Phys. **29**, 1667 (1958).

[23]B. J. Fontana, J. Chem. Phys. **31**, 148 (1959).

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Electronic mechanism of the high-temperature phase transitions in SmS and $Sm_{1-x}Gd_xS$

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The electronic mechanism of the phase transitions in $Sm_{1-x}Gd_xS$ [A. Yayaraman *et al.*, Phys. Rev. Lett. **31**, 700 (1973)] has been investigated by the x-ray *K*-line shift method [E. V. Petrovich *et al.*, Sov. Phys. JETP **34**, 935 (1972)] in a wide concentration and temperature range ($0 \leq x \leq 0.40$; $300 \lesssim T \lesssim 1000$ K). A smooth variation of the valency of samarium with increasing *x* has been observed at a high temperature, in contrast to the well-investigated discontinuous variation observed at room temperature [A. Yayaraman *et al.*, Phys. Rev. Lett. **31**, 700 (1973); V. A. Shaburov *et al.*, Sov. Phys. JETP **41**, 158 (1975)]. It has also been found that the valency of samarium increases in SmS and decreases in $Sm_{0.81}Gd_{0.19}S$ with increasing temperature. It is shown that the observed effects are due to the $4f \rightleftarrows$ band electron transition. The valency of samarium in SmS and $Sm_{0.81}Gd_{0.19}S$ varies in the range $300 \lesssim T \lesssim 1000$ K respectively from $m = 2$ to $m = 2.18 \pm 0.02$ and from $m = 2.42 \pm 0.02$ to $m = 2.27 \pm 0.02$. At $T \approx 1000$ K the valency of samarium increases in the region $0 \leq x \leq 0.40$ from $m = 2.18 \pm 0.02$ to $m = 2.62 \pm 0.02$. The dependences of the $Sm^{2+} \rightarrow Sm^{3+}$ transition energy on the gadolinium concentration and on temperature are computed under the assumption of thermal excitation of 4*f* electrons into the conduction band [B. C. Salest and D. K. Wohlleben, Phys. Rev. Lett. **35**, 1240 (1975)].

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INTRODUCTION

The isomorphic phase transitions in $Sm_{1-x}Gd_xS$ ($B \rightarrow M$ and $M \rightarrow B'$[1]) were investigated by the x-ray line shift method at room and liquid-nitrogen temperatures in our previous work.[2] We discovered that to the phase transitions correspond discontinuous changes in the energy of the x-ray *K* lines of samarium, changes which form a *V*-shaped "facsimile"[3] typical of 4*f* electrons and corresponding to changes in the valency of samarium due to $4f \rightleftarrows$ band electron transitions. In the transition from the semiconducting *B* phase to the metallized *M* phase ($x \gtrsim x_{cr} \approx 0.16$, $T \approx 300$ K) the valency of samarium increases discontinuously from $m = 2$ to the value $m = 2.62 \pm 0.03$; the transition from the *M* phase to the low-temperature intermediate *B'* phase ($0.16 \lesssim x \lesssim 0.22$, $T < 100$ K) is accompanied by a decrease in the valency of samarium (also discontinuously) from $m = 2.62 \pm 0.03$ to $m = 2.08 \pm 0.01$.[2]

Recently, Yayaraman and his co-workers[4] observed at high temperatures ($T > 400$ K) an abnormally larger thermal expansion of the crystal lattice of samples of $Sm_{1-x}Gd_xS$ of the intermediate composition: $0.16 \lesssim x \lesssim 0.22$. (The relative change in the lattice constant was $\Delta d/d \approx 2.3\%$ for $x = 0.18$ in the range $T \approx 300$–900 K.) Such a large thermal expansion of the *M* phase of $Sm_{1-x}Gd_xS$ is, in the opinion of these authors, due to the trapping of conduction electrons of samarian in the 4*f* states (i.e., to the 5*d*–4*f* transition) and, accordingly, to the change in the valency from $m \approx 2.8$ to $m \approx 2$.

The lattice constant of $Sm_{1-x}Gd_xS$ at a high temperature varies continuously. This circumstance makes it difficult to elucidate the mechanism of the effect and determine the changes in the valency from the crystallographic data, since the changes in the lattice constant due to the 5*d*–4*f* transition are maximized by the usual thermal expansion, which in a number of cases is substantial (e.g., in EuS and NdS the ratios $\Delta d/d \approx 1\%$ in the range $300 \lesssim T \lesssim 1000$ K[5]).

The purpose of the present paper is to elucidate by the x-ray *K*-line shift method the electronic mechanism of the high-temperature transition in SmS and $Sm_{1-x}Gd_xS$ and to determine the change in the valence state of the samarium atom in this transition.

RESULTS OF THE EXPERIMENT

In the experiment we measured the shifts of the x-ray *K* lines of samarium in $Sm_{1-x}Gd_xS$ ($0 \lesssim x \lesssim 0.40$) relative to the same lines of a reference Sms sample as a function of temperature and the gadolinium concentration. The measurements were performed on a special Cau-