

Metastable magnetic crystals

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Parameters are presented for a metastable crystal of an alkali metal which is composed of atoms with unidirectionally aligned spins, such as the distance between nearest neighbors, the sublimation energy, the Debye temperature, the change of energy accompanying spin reversal, the rate of evaporation of atoms from a surface, etc. The distance between nearest neighbors in the crystals under consideration considerably exceeds atomic dimensions, so that these ferromagnetic crystals are dielectrics. Analysis shows that they can be actually produced at a low temperature of the order of a few degrees Kelvin.

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1. The object of the present note is to draw attention to a peculiar physical object which, in our opinion, is of physical interest, and also may find practical application. Such an object is a crystal constructed of atoms of alkali metals whose electronic spins are all pointing in the same direction. If we consider a molecule consisting of two atoms of such a type with similarly directed spins it will turn out that for large distances between them the dependence of the potential energy of the interaction on the interatomic distance has a "well," i.e., formation of stable states of the molecule is possible. This is associated with the fact that at such distances the attractive potential corresponding to the interaction of induced moments becomes comparable with the potential of exchange repulsion due to overlapping of electron shells. Due to the weak interaction at large distances the dissociation energy of such a molecule is small compared to the dissociation energy of ordinary molecules.

Now let us construct a crystal from the atoms under consideration. The density of atoms in such a crystal will be small compared with ordinary crystals, and the crystal itself can exist only at low temperatures. The distance between nearest atoms considerably exceeds their size. Therefore all the electrons in the crystal under consideration "remain" in their own atoms, and the crystal is a dielectric. In this it differs in principle from metallic hydrogen which represents a combination of a proton lattice and a degenerate electron gas.^[1-5] In this case the distance between nearest nuclei in metallic hydrogen is a quantity of the order of atomic dimensions.

The crystal under consideration here is metastable since a spontaneous transition is possible for this crystal into a lower energy state corresponding to antiparallel spins of neighboring atoms. Another essential factor is the magnetic properties of such a crystal. The magnetic field produced by it in order of magnitude corresponds to the magnetic field of ferromagnetics.

2. The parameters of a metastable magnetic crystal are determined by the pair interaction between individual atoms. Therefore we first investigate the pair

interaction between two atoms of alkali metals. The interaction potential for two atoms in a 2S -state at distances between them large compared to their dimensions is composed of two parts:

$$U(R) = U_{l.r.}(R) \pm \frac{1}{2} \Delta(R). \quad (1)$$

The first term represents a long range interaction between atoms which corresponds to attraction and at large distances between nuclei can be written in the form of an asymptotic series

$$U_{l.r.}(R) = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}} - \frac{C_{12}}{R^{12}} - \dots, \quad (2)$$

where R is the distance between nuclei, the magnitudes of C_n are determined by the kind of interacting atoms. The second term in formula (1) describes the exchange interaction which is due to the overlapping of electronic orbits of interacting atoms. The minus sign in formula (1) corresponds to zero total spin of interacting atoms, the plus sign corresponds to total spin equal to unity. Below we consider this latter case when the spins of the interacting atoms point in the same direction. The potential of exchange interaction at large distances between the atoms can be represented in the form of the following asymptotic series:

$$\Delta(R) = BR^b e^{-aR} \left(1 + \frac{a}{\sqrt{R}} + \frac{b}{R} + \dots \right). \quad (3)$$

We note that in the case under consideration of the interaction between atoms with spins pointing in the same direction the potentials of the long range and the exchange interaction become comparable at large distances between the nuclei where the asymptotic expansions given for them are valid. Therefore these expansions will be used in subsequent discussion. The asymptotic methods for calculating interaction potentials are sufficiently well developed and are presented in monographs^[6,7].

Table I exhibits parameters for the interaction potentials between two atoms of hydrogen, of alkali metals and of metastable helium for large distances between them, while Table II exhibits parameters of a diatomic

TABLE I. Parameters of the interaction potentials of atoms (in atomic units).

Interacting atoms	H - H	Li - Li	Na - Na	K - K	Rb - Rb	Cs - Cs	He (2 ³ S) - He (2 ³ S) *
C_3 (sec ³)	6.5	1380	1580	3680	4350	6660	3300
C_3 (sec ³)	124.4	$8.4 \cdot 10^4$	$1.1 \cdot 10^5$	$4.5 \cdot 10^5$	$6.1 \cdot 10^5$	$1.1 \cdot 10^6$	$2 \cdot 10^5$
α	2	1.260	1.252	1.194	1.112	1.072	1.184
β	2.5	4.56	4.59	5.17	5.29	5.53	4.91
$B^2 \cdot 10$	1.65	0.027	0.025	0.006	0.0042	0.0021	0.013
a^{11}	1.92	3.82	3.85	4.48	4.60	4.87	4.20

*)Parameters for the exchange interaction potential between metastable helium atoms are quoted for the $^5\Sigma$ state.

molecule consisting of the atoms indicated above with spins pointing in the same direction. In the calculation of these parameters the first two terms of the asymptotic series for the potentials of the long range (2) and the exchange (3) interactions were taken into account. For comparison in Table II we have shown in brackets the values of the parameters calculated utilizing only the first term of the asymptotic expansion of the interaction potentials. The magnitude of the difference between these values characterizes the accuracy of the method used to calculate these quantities.

We shall dwell particularly on the case of the hydrogen molecule in the triplet state where an analysis of the accuracy of the results can be carried out most completely. According to the most accurate variational calculation of Kolos and Wolniewicz^[12] the depth of the potential well for the hydrogen molecule in the triplet state amounts to 6.2 °K. The accuracy of this calculation can be estimated in terms of the divergence of its result from the data of the asymptotic expansion for large distances between the nuclei, where the values of the interaction potentials are small. For a distance between the nuclei of $10a_0$ (a_0 is the Bohr radius) the potential for the exchange interaction between the atoms of hydrogen in accordance with the variation calculation of Kolos and Wolniewicz^[12] is equal to 0.76 °K. The first term of the asymptotic expansion for this quantity yields the value of 0.34 °K, two terms of the expansion yield 0.46 °K. As may be seen, the asymptotic series converges quite well and the divergence in this case should be ascribed to the inaccuracy of the variational calculation. From this we can estimate the accuracy of the variational calculation to amount to several tenths of a degree.

Utilizing the next terms of the asymptotic series for the potential of the long range interaction between two hydrogen atoms we can more accurately determine the

TABLE II. Parameters for diatomic molecules consisting of atoms with parallel spins.

Molecule	H ₂	Li ₂	Na ₂	K ₂	Rb ₂	Cs ₂	He ₂
Equilibrium internuclear distance, A	4.44 (4.50)	7.17 (6.62)	7.14 (6.55)	8.17 (7.73)	8.24 (7.92)	8.36 (8.09)	7.04 (6.90)
Dissociation energy, °K	4.1 (3.2)	46 (52)	54 (63)	63 (56)	74 (58)	100 (75)	103 (91)
Change in energy resulting from a reversal of spin of one of the atoms, °K	6.6 (4.5)	95 (120)	120 (150)	140 (120)	180 (130)	280 (180)	300 (240)

TABLE III. Parameters of gaseous crystals.

Atoms of the crystal	Equilibrium distance between nearest neighbors, A	Sublimation energy, °K	Debye temperature, °K	Density, g/cm ³
Li (2S)	7.15	290	80	0.05
Na (2S)	7.00	365	55	0.18
K (2S)	8.03	440	35	0.19
Rb (2S)	8.06	550	25	0.42
Cs (2S)	8.12	760	20	0.64
He (2 ³ S)	6.98	655	127	0.03
Ne (1S)	2.93	250	64	2.1
Ar (1S)	3.29	1160	80	2.9
Kr (1S)	3.66	1900	63	4.4
Xe (1S)	4.08	1560	55	5.0

depth of the potential well on the basis of the asymptotic method, and from the convergence of the series estimate the accuracy of the results so obtained. Appropriate calculations lead to a value of the depth of the potential well of 4.9 ± 0.8 °K. This makes it possible to estimate that the results for the interaction potential obtained on the basis of the asymptotic method are accurate to 20-30%.

3. We turn to the determination of parameters of metastable magnetic crystals. The distance between neighboring nuclei in such crystals, as has already been noted previously, is large compared to the characteristic dimensions of the atoms. Therefore the potential for the interaction of the atoms in a crystal is an additive function of the potentials of pair interaction. For the long range interaction this is associated with the validity of perturbation theory according to which the nonadditivity for the potential of long range interaction is manifested in higher orders of expansion in terms of a small parameter. The potential for the exchange interaction between atoms is determined by the distribution of electrons along the axis joining their nuclei. Since the distribution of electron density in an atom is not altered by a weak interaction in the crystal under investigation, then the potential for the exchange interaction of an atom with the atoms surrounding it is the sum of the potentials for the interaction with each of these atoms.

Thus, the existence of a small parameter in the crystal under consideration, which is associated with the smallness of the potential for the interaction between atoms, makes it similar to a gas. The structure of the given crystal corresponds to dense packing—to a face-centered crystal when each atom has 12 nearest neighbors. Table III exhibits parameters of the crystals under investigation calculated on the basis of the previously introduced potentials for pair interaction. The method of carrying out the calculation has been described, for example, in the book^[13]. The energy of the zero-point oscillations of the nuclei—the Debye temperature—was calculated on the assumption that it is considerably lower than the sublimation energy which represents the energy of rupture of all the couplings in the crystal divided by the number of atoms. As may be seen from Table III this condition turns out to be satisfied for the objects under investigation. For comparison in Table III we have included parameters of crystals of an inert gas calculated by an analogous

TABLE IV.

Atoms of the metastable crystal.	Li	Na	K	Rb	Cs	He (2 ³ S)
Change in energy due to reversal of the spin of one of the atoms, 10 ³ °K	1.2	1.8	2.0	2.9	4.4	3.9
Surface tension dyn/cm	3.9	5.3	4.8	5.9	8.0	9.4

method in^[14] utilizing asymptotic expressions for the potentials of interaction between atoms.

Table III does not include hydrogen, because for it the calculated values of the energy of zero-point oscillations exceed the depth of the potential well in the crystal. Special calculations^[15] which have been carried out for a system consisting of hydrogen atoms or of atoms of its isotopes with spins pointing in the same direction have shown that such hydrogen and deuterium remain gases at any temperature. But tritium may become liquid at low temperatures with a binding energy of approximately 0.75 °K per atom. In carrying this out results were utilized of the variational calculation^[12] for the potential of the pair interaction of two hydrogen atoms. This calculation, as has been shown earlier, gives an overestimate for the depth of the potential well for the pair interaction between atoms.

Thus, the system of hydrogen atoms with spins pointing in the same direction does not form a bound crystalline state, since the potential well describing the attraction between atoms is too shallow, and for a low nuclear mass does not contain a single discrete level. For this reason we exclude hydrogen from further consideration.

4. An important place among the properties of a metastable magnetic crystal is occupied by its stability. The crystal under consideration can be destroyed if the spin of some of its atoms is reversed. This can occur under the action of an alternating magnetic field, but the frequency of this field cannot be small, since otherwise the reversal of spin of a single atom turns out to be adiabatically of low probability. The order of magnitude of the frequency of such a field which effectively destroys the crystal can be estimated from the change in the electron energy resulting from a reversal of the spin of an individual atom if the configuration of the crystal is preserved. This characteristic is exhibited in Table IV.

TABLE V. Density of saturated vapors above the crystal surface, cm⁻³

T, °K	Atoms of the crystal					
	Li	Na	K	Rb	Cs	He (2 ³ S)
4	3·10 ⁶	10 ²	7·10 ⁻³	6·10 ⁻⁹	10 ⁻²⁰	10 ⁻¹⁴
6	2·10 ¹¹	10 ⁷	4·10 ⁵	40	8·10 ⁻⁷	8·10 ⁻³
8	3·10 ¹³	9·10 ¹¹	4·10 ⁹	2·10 ⁶	4	6·10 ³
10	10 ¹⁵	7·10 ¹³	7·10 ¹¹	2·10 ⁹	3·10 ⁴	2·10 ⁷
12	10 ¹⁶	2·10 ¹⁵	3·10 ¹³	3·10 ¹⁰	2·10 ⁷	4·10 ⁹
14	7·10 ¹⁶	10 ¹⁶	4·10 ¹⁴	5·10 ¹²	2·10 ⁹	2·10 ¹¹

TABLE VI. Lifetime of an atom with respect to evaporation from the crystal surface, sec.

T, °K	Atoms of the crystal					
	Li	Na	K	Rb	Cs	He (2 ³ S)
4	10 ⁸	4·10 ⁷	9·10 ¹¹	10 ¹⁸	5·10 ²⁹	10 ²³
6	10 ⁻²	8	10 ⁴	10 ⁶	7·10 ¹⁵	2·10 ¹¹
8	3·10 ⁻⁵	4·10 ⁻³	1	2·10 ³	10 ⁹	2·10 ⁵
10	10 ⁻⁶	5·10 ⁻⁵	4·10 ⁻³	2	10 ⁵	60
12	10 ⁻⁷	2·10 ⁻⁵	10 ⁻⁴	2·10 ⁻²	2·10 ²	0,3
14	2·10 ⁻⁸	2·10 ⁻⁷	6·10 ⁻⁶	10 ⁻³	2	5·10 ⁻³

Metastable crystals can exist at low temperatures. Therefore parameters associated with the evaporation of crystals are significant. We shall assume that the binding energy of an atom situated on the surface of a crystal is equal to half of the sublimation energy. The coefficient of surface tension corresponding to this is shown in Table IV.

We discuss the evaporation of an atom from the surface of a crystal on the basis of a model proposed by Frenkel.^[16] The frequency of evaporation of an individual atom is equal to

$$\frac{1}{\tau} = \frac{\omega}{2\pi} e^{-U_0/T}, \quad (4)$$

where ω is the frequency of oscillation of the atom, U_0 is the binding energy of the atom on the surface which is taken to be equal to half the sublimation energy, T is the temperature. From this the flux of evaporating atoms is equal to

$$j = \frac{1}{\tau r_0^2}, \quad (5)$$

where r_0 is the distance between nearest neighbors. If over the surface of the crystal there is present a gas of atomic density N , then the flux of atoms to the surface is equal to

$$j = N \sqrt{\frac{T}{2\pi m}}, \quad (6)$$

where m is the mass of the atom.

Table V shows the temperature dependence of the saturated vapor pressure over the surface of the crystal for the types of metastable crystals under consideration. These quantities are obtained from the equality of the fluxes presented above. Moreover Table VI exhibits the lifetimes for atoms situated on the surface of the crystal with respect to their evaporation. These data give us an idea of the stability of the solid phase of metastable crystals. They make no pretence of being particularly accurate and are valid only as to order of magnitude, since in the temperature range under consideration they are very sensitive to the value of the sublimation energy determined with an accuracy of ~20–30%. As may be seen, metastable magnetic crystals can exist stably at a temperature of several degrees.

5. One of the principal problems is the production of the crystals under consideration. Apparently, the simplest method of producing them might be the deposition

of cold polarized beams of atoms on a cooled surface in an external magnetic field. Such a surface should be composed of only spinless atoms and molecules. As an example of such a surface we mention a crystal of an inert gas, of molecular nitrogen or of hydrogen. At present it is possible to obtain sufficiently intense polarized beams of atoms. As an example supporting such possibilities we refer to experiments^[17,18] carried out several years ago. In them on the basis of the method of intersecting beams a measurement was made of the differential cross section for the scattering of two atoms of alkali metals with spins pointing in the same direction. The intensity of the beams turned out to be sufficient to deduce on the basis of these cross sections the parameters for the potential of interaction between two atoms of alkali metals in the triplet state.

Of course, availability of intense polarized beams is not yet sufficient for the production of metastable magnetic crystals. Imagination and inventiveness will be required, and in the long run on this will depend the extent to which such metastable crystals can become serious physical objects.

We note one circumstance. We have considered magnetic crystals the basis for which consists of atoms in 2S -states. Hyperfine states of atoms, which can themselves be of interest, affect neither the investigated properties nor the method of production of metastable magnetic crystals.

At the present time it is difficult to discuss the possibilities of the crystals under consideration. They can be utilized as counters for fluxes of particles, particularly of polarized ones. It is possible that on the basis of metastable magnetic crystals by utilizing the hyperfine states of atoms one might succeed in producing good frequency standards or memory devices. Crystals of metastable helium can be sources of energy for cosmic purposes—their stored energy amounts to approximately 500 kJ/g. These assertions contain more fantasy than certainty, and therefore at present it is premature to discuss this topic, but one should regard the metastable crystals under consideration as

physical objects. Undoubtedly metastable magnetic crystals are amusing physical objects. Whether they can become interesting physical objects will only be shown by further investigations. And the object of the present note is to stimulate such investigations.

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