ISOTOPE EFFECTS IN THE STRUCTURAL PROPERTIES OF SOLIDS

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CONTENTS

INTRODUCTION

STUDIES of the structures of a number of chemical compounds,[1-7,14,16] have shown that the replacement of hydrogen by deuterium in them leads to appreciable changes in the lattice parameters. The direction of this isotope effect, as a rule, amounts to a decrease in the lattice parameters from the hydrogen to the deuterium compound. However, the converse situation has occurred in individual cases.[13-16]

In a number of cases, the isotope effect in the lattice parameters was found to be temperature-dependent, owing to a difference in the linear expansion coefficients of the hydrogen and deuterium compounds. Most often, deuteration increases the expansion coefficient.[1,2] For certain substances which undergo polymorphic transitions as the temperature varies, isotope substitution shifts the temperatures of these transitions[11,12,37,40,41,45], and sometimes even alters the nature of the transition.[11,41]

During the last thirty years, a considerable number of attempts have been made to explain the above-mentioned isotope effects in the structural properties of solids. However, there is still no unified viewpoint on their nature. Perhaps the difficulties in explaining these isotope effects are particularly due to the fact that these effects have been discovered and studied in complex compounds. Only in the last few years has it become possible to study isotope effects in the structural properties of pure elements.[58,61,69,80,84,86,88,89,93] On the one hand, this has resulted from advances in

methods of preparing pure isotopes, and on the other, from advances in methods of structural research. Naturally, the isotope effects could first be found and studied in the light elements, such as hydrogen,[61,80] helium,[84,86] and lithium,[58,89] whose isotopes have large relative mass differences. Subsequently, these studies have been extended to heavier elements, for which the relative mass differences of the isotopes do not exceed 10% (Ne, Ni).[88,93]

This review will give as full as possible a collection and discussion of the published results of experimental and theoretical studies of isotope effects in the structural properties of solids.

I. CHANGES IN THE UNIT-CELL VOLUMES OF CHEMICAL COMPOUNDS PRODUCED BY SUBSTITUTION OF HEAVIER FOR LIGHTER ISOTOPES

The first attempt to find a difference in the structures of solids differing in isotopic composition was made as early as 1934. Megaw [1] published a study in that year, describing the results of an x-ray diffraction study of ordinary and heavy ice. Rotation patterns of single crystals of ice were taken with monochromatic CuKα and CoKα radiation at temperatures of −66° and 0°C (heavy-ice patterns were also taken at +4°C). At these temperatures, both types of ice have a hexagonal lattice with an axial ratio c/a = 1.63. At −66°C, the lattice parameters along the c axis of heavy and ordinary ice turned out to be the

same (c = 7.338 ± 0.0035 kX), while the a-axis para-
meters at this temperature differed by ~ 0.1% (a_{H_2O}
= 4.5085 ± 0.002 kX; a_{D_2O} = 4.5055 ± 0.002 kX). At
0°C, both parameters were somewhat greater for
heavy than for light ice: a_{H_2O} = 4.5135 ± 0.0014 kX;
c_{H_2O} = 7.3521 ± 0.0012 kX; a_{D_2O} = 4.5165 ± 0.0012 kX;
c_{D_2O} = 7.3537 ± 0.0012 kX. The molar volume ratio
at 0°C was: V_{D_2O}/V_{H_2O} = 1.0014.

Later x-ray diffraction studies of heavy and or-
dinary ice [2] have given results slightly differing
quantitatively from Megaw's original data, but agree-
ing in the fundamental result that the unit-cell volume
of ordinary ice at low temperatures is about 0.1%
larger than that of heavy ice (at −185°C, a_{H_2O} = a_{D_2O}
= 4.470 Å; c_{H_2O} = 7.301 Å; c_{D_2O} = 7.293 Å).

Historically, the study of heavy and ordinary ice
was followed by a comparison of the structures of the
isotopically-substituted lithium hydrides LiH and
LiD. [3] In the ice structure, hydrogen constitutes
part of the group of atoms forming a water molecule;
the isotopic substitution brings about small changes
in the internuclear distances within this group, but
has little effect on the intermolecular distances, and
hence on the lattice parameters. In distinction from
ice, the hydrogen atoms in lithium hydride (or deuter-
ium atoms) occupy their own special positions at
sites in an NaCl-type structure. Thus, isotopic sub-
stitution here changes the unit-cell dimensions more
significantly than in ice: a_{LiH} = 4.085 ± 0.001 kX;
a_{LiD} = 4.065 ± 0.001 kX. That is, the discrepancy in
lattice parameters between LiH and LiD amounts to
0.5%. Even larger lattice-parameter contractions
upon replacing hydrogen by deuterium have been
found in hydrogen sulfide and hydrogen selenide (with
2.55% and 4.5% volume contraction, respectively) [4],
and in hafnium hydride[5] (for which the difference in
molar volumes is 1.7%). Hafnium hydride has a body-
centered tetragonal lattice, with two molecules of
HfH_2 in the unit cell. The axial ratios of the tetra-
gonal cells of HfH_2 and HfD_2 are 1.254 and 1.257,
respectively. The parameters are: a_{HfH_2} = 3.478
± 0.004 Å; c_{HfH_2} = 4.363 ± 0.001 Å; a_{HfD_2} = 3.456
± 0.003 Å; c_{HfD_2} = 4.345 ± 0.003 Å. The Hf-Hf dis-
tances in the HfH_2 and HfD_2 structures are 3.287
and 3.270 Å, respectively. The Hf-H and Hf-D dis-
tances in these structures are 2.053 and 2.041 Å.

Somewhat smaller differences in molar volumes
have been found in the metal-like deuterides and hy-
drides of uranium ($\Delta V/V$ = 0.5%) [6] and lanthanum
($\Delta V/V$ = 0.2%).[7] Uranium hydride has a cubic struc-
ture of the β-tungsten type (a_{UH_3} = 6.631 ± 0.0008 Å;
a_{UD_3} = 6.620 ± 0.002 Å). The lanthanum hydrides
have face-centered cubic lattices (the parameters
for LaH_2 and LaH_3 are 5.662 and 5.695 Å, respec-
tively, while those of the deuterides LaD_2 and LaD_3
are 5.658 and 5.691 Å).

The distance of the nitrogen nucleus from the plane
of the hydrogen nuclei in the ammonia molecule has

been shown to change upon deuteration from the change
in the dipole moment, [8] and later by direct x-ray
diffraction measurements. [2] At −185°C, the lattice
parameter of cubic NH_3 is 5.2253 Å, while that of
ND_3 is 5.2153 Å.

The literature furnishes information on the lattice
parameters of several pairs of ammonium halides
differing in isotopic composition (NH_4Cl and ND_4Cl;
NH_4Br and ND_4Br; NH_4I and ND_4I).

A characteristic of all these compounds is the oc-
currence of low-temperature polymorphic transitions,
the major feature for which they have been studied.
These studies also provide us with data on the isotope
effect in the lattice parameters of these compounds.

The values of the lattice parameters at +18°, −78°,
and −185°C are 3.868$_4$, 3.834$_3$, and 3.820$_0$ Å respec-
tively for NH_4Cl; and 3.868$_2$, 3.8370, and 3.819$_0$ Å
for ND_4Cl.[9] The isotope effect in the lattice parame-
ter changes sign somewhere in the neighborhood of
−150°C. Below this temperature, as is the usual case,
the lattice parameter of the hydrogen compound is
larger than that of the deuterium compound, while the
converse is true above this temperature. In the high-
temperature modification (the transition temperatures
of these compounds occur at about −30°C), the isotope
effect regains its normal sign. Actually, at 18°C the
size of this effect does not exceed the errors of
measurement.

The compounds NH_4Br and ND_4Br [10-12] undergo
polymorphic transitions at −39° and −58°C, respec-
tively. The high-temperature modifications of both
compounds have cubic structures of the CsCl type,
while the low-temperature modifications are tetra-
gonal. In the high-temperature phase, the molar
volumes of these compounds (Table I) [12] differ by
0.5%, while in the low-temperature phase they are
approximately equal.

Table I.

	Parameter a, Å		Molar volume, cm³	
	−30° C	−73° C	−30° C	−73° C
	Cubic	Tetragonal	Cubic	Tetragonal
NH_4Br	4.041	4.034	40.00	39.78
ND_4Br	4.034	4.034	39.78	39.74

The compounds NH_4I and ND_4I [12] have been stud-
ied over the temperature range from −70° to −40°C,
a range through which a polymorphic transition ex-
tends. Throughout this range the molar volume of
NH_4I is about 0.2% larger than that of ND_4I.

In contrast to all the compounds discussed above,
replacement of hydrogen by deuterium in acid salts
increases the unit-cell dimensions, as a rule.

Thus, the scattering angles obtained from rotation
patterns taken from single crystals of KH_2AsO_4 and
KD_2AsO_4 [13] (which are tetragonal) were compared.

It was found that all the zero-layer diffraction spots having large sums of indices occurred at appreciably larger scattering angles in the hydrogen compound (θ_H) than in the deuterium compound (θ_D).

If one converts the values of $\Delta\theta = \theta_H - \theta_D$ for different diffraction spots to the relative differences in the corresponding interplanar spacings, $\Delta d/d = -\Delta \sin\theta/\sin\theta = \alpha$, one finds that these quantities are highly anisotropic. The direction of the maximum isotope effect practically coincides with the direction of the short hydrogen bonds in the crystal. The entire magnitude of this effect was accounted for by stretching of these bonds by 0.0080 kX.

Analogous measurements and calculations give the stretching of the short hydrogen bonds in the isomorphous compounds KH_2PO_4 [13,14] and $NH_4H_2PO_4$ [13,15] as 0.0097 and 0.100 kX, respectively. In the compounds KH_2PO_4 and $NH_4H_2PO_4$, the expansion along one of the axes is accompanied by a small Poisson contraction in the perpendicular direction.

The difference in the sizes of the isotope effect for KH_2AsO_4 and KH_2PO_4 agrees with the difference in the binding strengths of the protons in the molecules of these compounds, and hence, with the difference in their hydrogen-bond lengths. The larger isotope effect in KH_2PO_4 corresponds to larger forces and shorter length of the hydrogen bonds (in KH_2PO_4 they are 2.52 Å long, but 2.54 Å long in KH_2AsO_4).

It is interesting to note that the binding forces in the KH_2PO_4 structure are so disturbed by substitution of deuterium for hydrogen that KD_2PO_4 crystallizes in a new structure, which is apparently an unstable form of this salt. In order to prepare the tetragonal modification of KD_2PO_4, isomorphous with the form of KH_2PO_4 stable at room temperature, it was necessary to take special measures, in particular the deposition of KD_2PO_4 from its solution in D_2O on crystals of tetragonal KH_2PO_4. [14]

The compounds $NaHCO_3$ and $NaDCO_3$ [16] have been studied in powder form by X-ray diffraction with nickel-filtered $CuK\alpha$ radiation. The diffraction lines obtained for angles $\theta > 70°$ were, as a rule, shifted appreciably to smaller angles for $NaDCO_3$ than for $NaHCO_3$ (the Bragg angles were: $\theta_H = 80.81°$, $79.90°$, $76.08°$, $75.46°$, $73.31°$, $72.80°$, with differences in angle $\Delta\theta = \theta_H - \theta_D$, respectively of: $-0.06°$, $-0.12°$, $+0.24°$, $+0.24°$, $+0.27°$, $+0.26°$).

A positive value of $\Delta\theta$ means that the interplanar spacings increase upon replacement of hydrogen by deuterium, just as in the other acid salts.

The results obtained from an x-ray diffraction analysis of $NaHSO_4$ and $NaDSO_4$ [14] are so indefinite, owing to lack of knowledge of the structures of these salts, that it is difficult to determine the size of the isotope effect.

In addition to the acid salts mentioned above, whose structures contain hydrogen bonds between oxygen atoms, the acid salts KHF_2 and KDF_2 [14] have been studied in order to obtain information on hydrogen bonds between other atoms. The isotope effect in the interplanar spacings of KHF_2 has a sign opposite to that of the other acid salts discussed in this section.

For diffraction maxima occurring at angles $\theta_H \cong 82°$, we find that $\Delta\theta = \theta_H - \theta_D = -0.12°$. That is, $\theta_D > \theta_H$; thus the interplanar spacings in the deuterium compound are somewhat smaller than in the hydrogen compound.

X-ray diffraction analyses have also been made of several pairs of organic compounds in which the carboxyl or hydroxyl groups differ in isotope composition (by containing hydrogen or deuterium). The compounds studied were

α-and β-resorcinol: $C_6H_4(OH)_2$ and $C_6H_4(OD)_2$ [16],

pentaerythritol: $C(CH_2OH)_4$ and $C(CH_2OD)_4$ [14],

oxalic acid dihydrate: $(COOH)_2 \cdot 2H_2O$ and $(COOD)_2 \cdot 2D_2O$ [16],

phthalic acid: $C_6H_4(COOH)_2$ and $C_6H_4(COOD)_2$ [16],

benzoic acid: $C_6H_5(COOH)_2$ and $C_6H_5(COOD)_2$ [16],

succinic acid: $C_2H_4(COOH)_2$ and $C_2H_4(COOD)_2$ [16],

fumaric acid: $(CH_2)_2(COOH)_2$ and $(CH_2)_2(COOD)_2$ [14].

In all these compounds, the sign of the isotope effect amounts to an increase in the unit-cell dimensions upon replacement of hydrogen by deuterium. Among them, only oxalic acid dihydrate showed a large isotope effect, while for the other compounds it was an order of magnitude smaller and phthalic acid showed no effect within the experimental accuracy.

For oxalic acid dihydrate, the monoclinic lattice parameters of $(COOH)_2 \cdot 2H_2O$ are a = 6.120 ± 0.02 Å; b = 3.600 ± 0.001 Å; c = 12.030 ± 0.03 Å, and β = 106°12'. Thus, from these known parameters and from the shifts in $h00$ and $00l$ type reflections, the lengths of the a and c axes of the monoclinic unit cell of $(COOD)_2 \cdot 2D_2O$ were determined to be 6.149 and 12.071 Å, respectively.

The values of $\Delta\theta = \theta_H - \theta_D$ and the corresponding values of $\alpha = \Delta d/d$ determined for planes having normals in the (010) plane and forming various angles ξ with the c axis (see Fig. 1a) show that the isotope effect is quite anisotropic.

By comparing the angular dependence of the isotope effect in the (010) plane with the atomic arrangement in that plane (see Fig. 1b), the authors drew the conclusion that the short hydrogen bonds (2.52 Å long) are lengthened by replacing the hydrogen with deuterium by 0.0054 Å per unit length. The hydroxyl bonds of lengths 2.87 and 2.84 Å are slightly shortened thereby.

Just as for the acid salts, a study has been made of a pair of organic substances differing in isotopic composition, in which the hydrogen bonds involve atoms other than oxygen. In this case, urea [CO $(NH_2)_2$ and $CO(ND_2)_2$] was studied. [14] Just like
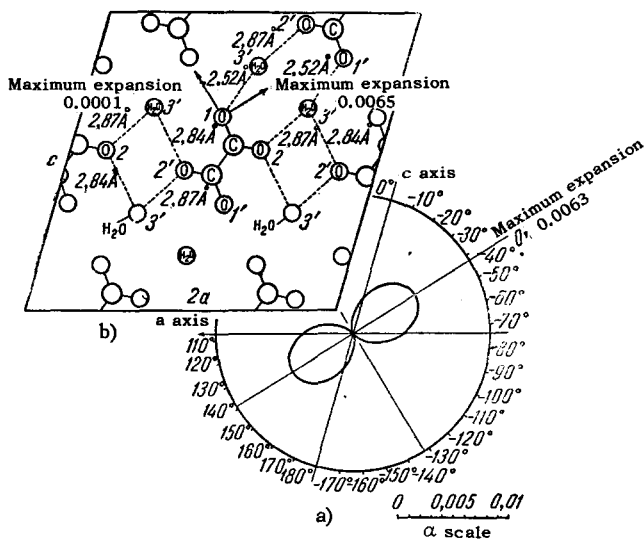
FIG. 1. The isotope effect in the (010) plane of $(COOH)_2 \cdot 2H_2O$ and the atomic arrangement in this plane.

KHF$_2$, urea had an isotope effect of sign opposite to that of the other organic compounds discussed above. The diffraction lines observed at angles $\theta \cong 74°$ were shifted to larger angles in the deuterium compound: $\theta_D > \theta_H$ ($\theta_H - \theta_D = -0.09°$). That is, the lattice contracts slightly upon replacement of H by D.

Only one study [17] is known in which an isotope effect has been studied involving the replacement of an element heavier than hydrogen in a compound. This was a study of the isotope effect in the lattice parameter of face-centered cubic LiF upon replacement of the atoms of the light isotope of lithium (Li^6) by atoms of the heavier isotope (Li^7).

The mean values of the parameters for Li^{6}F and Li^{7}F at 25°C, as calculated from the x-ray diffraction patterns of eight independent specimens of each of these compounds were 4.02710 Å for Li^{6}F and 4.02628 Å for Li^{7}F. That is, the lattice parameter for the compound with the lighter lithium isotope was 0.0008 Å larger than for the compound with the heavier isotope ($\Delta a/a = 2 \times 10^{-4}$).

In the structures of inorganic and organic compounds, the hydrogen atoms form covalent or ionic bonds with the atoms of the other constituents. On the other hand, in solid solutions in metals, hydrogen occurs in the "metallic" state, as it were. It dissolves as atoms and is partially ionized. [18] Although the hydrogen atoms are so small (Bohr radius 0.53 Å) that they can be completely fitted within the interstices of the metal structure without deforming it, they nevertheless bring about a lattice expansion. This involves the fact that "metallic" hydrogen is stable with respect to covalent hydrogen only at lattice parameters corresponding to pressures not less than 2.5×10^5 atm.[19] The expansion of the metal lattice by the incorporated hydrogen gives rise to the

necessary internal pressure. Thus, palladium, which has a compressibility of 0.4×10^{-6} atm^{-1}, increases in volume upon dissolving hydrogen by about 10%, which just corresponds to a pressure of 2.5×10^5 atm.[20]

The lattice expansion of palladium in hydride formation differs upon solution of hydrogen and deuterium. An x-ray diffraction study of a palladium strip saturated in an electrolytic bath with hydrogen (or deuterium) showed that the lattice parameter of of the palladium (a = 3.8821 Å) is increased by solution of hydrogen by 0.1430 ± 0.0004 Å, but by solution of deuterium by 0.1325 ± 0.004 Å.[21] The volume increase of the metal due to solution of hydrogen or deuterium amounts to 11.46% or 10.59%, respectively.

Characteristically, the solubility of deuterium in palladium is somewhat higher than that of hydrogen. The concentration of dissolved atoms (c = H/Pd), as determined by measuring the electrical resistance at 0°C, was 0.74—0.81 for hydrogen, and ~ 0.9 for deuterium. That is, the solubility of deuterium in palladium is about 10% greater than that of hydrogen.

The converse phenomenon has been observed in the solution of hydrogen and deuterium in nickel [22] and iron.[23] These metals were saturated with hydrogen (or deuterium) by passing a current of gas over the powdered metals at 1000°C. It was found here that the solubility of deuterium is 10% lower than that of hydrogen.

The isotope effect in the values of the lattice parameters of crystals containing ordinary and heavy water of hydration is very small. No difference in lattice parameters has been found between KAl(SO$_4$)$_2$ $\cdot$12H$_2$O and KAl(SO$_4$)$_2 \cdot$12D$_2$O; UO$_2$(NO$_3$)$_2 \cdot$6H$_2$O and UO$_2$(NO$_3$)$_2 \cdot$6D$_2$O; or KCr(SeO$_4$)$_2 \cdot$12H$_2$O and KCr(SeO$_4$)$_2 \cdot$12D$_2$O. [24] A very small contraction has been shown by the rotation-pattern method upon replacing the H$_2$O by D$_2$O in CuSO$_4 \cdot$5H$_2$O.[14] The difference in x-ray diffraction angles for SrCl$_2 \cdot$6H$_2$O and SrCl$_2$ 6D$_2$O amounts to ~ 0.2° at θ = 84°, with θ_H > θ_D. That is, the lattice is expanded upon replacement of the H$_2$O by D$_2$O, with $\Delta V/V \cong 10^{-4}$ (see[14]).

II. TEMPERATURE-DEPENDENCE OF ISOTOPE EFFECTS IN THE LATTICE PARAMETERS AND SHIFTS IN PHASE-TRANSITION TEMPERATURES IN DEUTERATED COMPOUNDS

It is reasonable to limit the discussion of the temperature-dependence of the isotope effect in the lattice parameters to the data on ice, resorcinol, oxalic acid dihydrate, and NH$_4$Cl (the other ammonium halides have been studied at different temperatures only with regard to polymorphic transitions, and the data on their lattice parameters at different temperatures refer to different modifications, and hence are not comparable). If we limit ourselves to the temper-

tures −66° and 0°C, at which H_2O and D_2O were studied in one of the papers,[1] we can conclude that the volume coefficient of thermal expansion over the temperature range from −66° to 0°C is larger for heavy ice than for ordinary ice:

$$\beta_{H_2O} = 6.3 \cdot 10^{-5}, \quad \beta_{D_2O} = 10.7 \cdot 10^{-5}.$$

The difference in linear expansion coefficients of H_2O and D_2O leads to an inversion in the isotope effect in the lattice parameters. The inversion point for the a axis occurs between −66° and 0°C, while it apparently lies near −66°C for the c axis. A comparison of the lattice parameters of NH_4Cl and ND_4Cl at −78° and −185°C shows that, in this temperature range, the linear expansion coefficient of the H compound is 3.5×10^{-5}, while that of the D compound is 5.5×10^{-5}. Owing to this considerable difference in the linear expansion coefficients, the isotope effect $\Delta a = a_H - a_D$ changes sign between −185° and −78°C, varying from +0.0010 Å at −185°C to −0.0027 Å at −78°C.

In contrast to ice and NH_4Cl, for α-resorcinol the thermal expansion coefficient of the deuterium compound is lower than that of the hydrogen compound. There is certain anisotropy observed in its magnitude. For both compounds, $C_6H_4(OH)_2$ and $C_6H_4(OD)_2$, the maximum expansion coincides with the b axis of the unit cell, while the minimum coincides with the a axis.

For oxalic acid dihydrate, the direction of maximum expansion not only does not coincide with any of the crystallographic axes of the lattice, but is even somewhat different in the $(COOD)_2 \cdot 2D_2O$ structure from that in the $(COOH)_2 \cdot 2H_2O$ structure.

The direction of maximum expansion lies in the (010) plane between the c axis and the direction of maximum isotope effect, which forms an angle of −40° with the c axis. In the direction of maximum expansion, we find on heating from 90° to 290°K,

$$\alpha_{H_{max}} = \frac{\Delta l_{max}}{l} = 0.0110, \quad \alpha_{D_{max}} = \frac{\Delta l_{max}}{l} = 0.0114.$$

In the direction normal to the direction of maximum expansion, both compounds show a small rela-

tive contraction of the lattice with increasing temperature.

In the ammonium halide series,[10,26] phase transitions occur as the temperature varies, and the effect of deuteration on the position and nature of these phase transitions has been studied.

Studies performed on the H- and D-ammonium halides have shown that isotope substitution not only shifts (sometimes by tens of degrees) the phase transition temperatures, but even changes their nature. Thus, the replacement of hydrogen by deuterium in the NH_4Cl structure [37,40,41] (Fig. 2) shifts the transition temperature 7° upward (from −30.5° to −23.5°C). The transition is broadened, being transformed from an abrupt transition into a continuous one, and the hysteresis disappears (or at least, the temperature lag is narrowed within the limits of observability). The replacement of hydrogen by deuterium in the NH_4I structure [12] also increases the diffuseness, but this time the transition is shifted to lower temperatures. While the transition in NH_4I extends continuously over a range of ~20°, in ND_4I it extends over an interval one or two degrees wider. The minimum in the molar volume-temperature curve is displaced from −39°C (for NH_4I) to −43°C (for ND_4I). The maximum in this curve is shifted downward by about 3°C (Fig. 3).

The transition curve undergoes especially sharp alterations upon replacement of H by D in the compound NH_4Br.[11]

The transition from the cubic to the tetragonal modification is shifted from −39°C (for NH_4Br) to −58°C (for ND_4Br), the hysteresis band is somewhat broadened (from 0.06° to 0.15°), and the change in molar volume accompanying the transition is somewhat increased (0.06 cm^3 for NH_4Br, but 0.17 cm^3 for ND_4Br).

In addition to the low-temperature phase transition at −58°C, ND_4Br shows another phase transition at −114°C.[11] This transition is accompanied by a change in molar volume of −1.08 cm^3, and exhibits a hysteresis band of 9° width (the transition takes place in the vicinity of −105°C on heating; see Fig. 4). In-
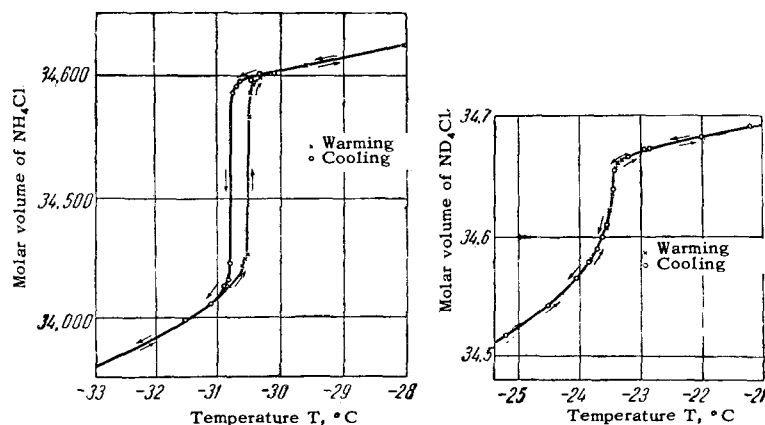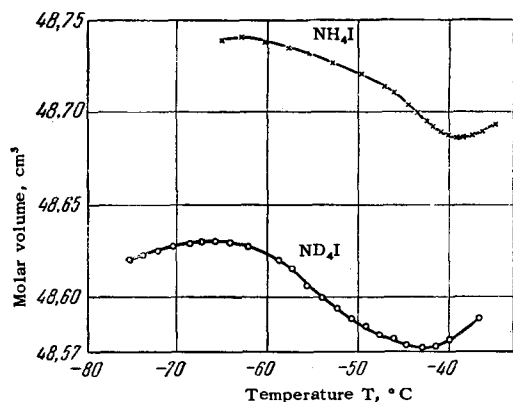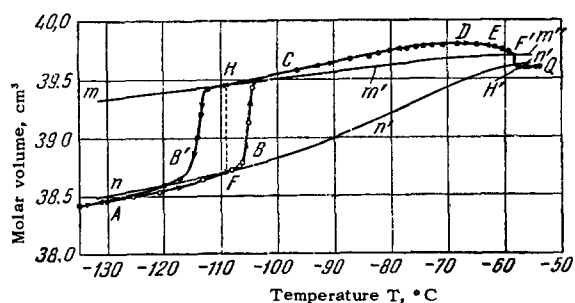

FIG. 2. Low-temperature transitions in NH_4Cl and ND_4Cl.

FIG. 3. Low-temperature transitions in NH_4I and ND_4I.

FIG. 4. Low-temperature transition in ND_4Br.

terestingly, this second transition results in re-for-mation of a cubic phase, identical with the high-tem-perature phase both from x-ray diffraction data [11] and from piezoelectric measurements. [42] This transi-tion, in which the phase stable at high temperatures is restored on lowering the temperature, has been termed a retrograde transition.

For some time, it was considered that there is no analogous phase transition from the tetragonal to the cubic structure in NH_4Br. It was found [43] in 1952 for this compound as well, but at a temperature 62° lower.

Besides the data on the low-temperature phase transitions of the H- and D-ammonium halides, there are data [44] showing that replacement of hydro-gen by deuterium in the compound ($NH_4)_2SO_4$ shifts the phase transition point upward from −49.7°C by approximately 0.5°. The transition on heating takes place with a volume decrease. The shift in the phase-transition point is especially large in the replacement

of H by D in the potassium acid phosphate KH_2PO_4. The H compound transforms at 123°K from the high-temperature tetragonal modification to the low-tem-perature orthorhombic modification, which is ferro-electric. In the D compound, this transition takes place at a temperature almost 100° higher (at 213°K). [45]

As was mentioned above, in addition to the tetra-gonal structure stable at room temperature, KD_2PO_4 possesses another unstable modification. This com-pound crystallizes in the latter form from solution, and transforms to the stable tetragonal modification only after long standing. [15] The structure of this metastable modification has been determined [46] to be monoclinic, with parameters a = 7.37 ± 0.01 Å, b = 14.73 ± 0.01 Å, c = 7.17 ± 0.01 Å, and β = 92°

Spectroscopic measurements [47] have shown that the phase transitions in the ammonium halides involve a change in the nature of the orientational order of these ions, as was proposed as early as 1936 by J. I. Frenkel. [48] This was subsequently confirmed by direct neutron diffraction measurements. [49-52]

In all the phases, the halide ions are arranged at the vertices of the cube, while the ammonium tetra-hedra are located on the cube faces (in the high-tem-perature α-phase) or the center of the cube (in the low-temperature phases). Neutron-diffraction analy-sis has made possible the establishment of the exist-ence of three low-temperature phases, β, γ, and δ, differing in the arrangement of the hydrogen atoms in the ammonium tetrahedra. In the δ-phase, the am-monium tetrahedra are oriented in parallel in all cells. In the γ-phase they are antiparallel in neigh-boring cells, and the lattice can be described as tetra-gonal. In the β-phase, the ammonium tetrahedra are oriented at random.

Data on the phase transitions of the ammonium halides are given in Table II.

It is interesting to note that deuteration shifts the transition temperatures in the same direction as pressure does. [56]

Measurements of the heat capacities of the am-monium halides under pressure were carried out be-fore the war in the Khar'kov Cryogenic Laboratory, [29,30] and showed that the transition temperature for NH_4Cl increases from 243°K at zero kg/cm² to 256°K at 1425 kg/cm², while the transition tempera-

Table II. Transition temperature, °K

Salt \ Transition	$\alpha \to \beta$	$\beta \to \gamma$	$\beta \to \delta$	$\gamma \to \delta$
NH_4Cl	458 [53]	—	243 [38]	—
ND_4Cl	—	—	249 [41]	—
NH_4Br	411 [54]	235 [21]	—	100 [43]
ND_4Br	398 [49]	215 [49]	—	169 [43]
NH_4I	257 [55]	231 [55]	—	—
ND_4I	254 [12]	227 [12]	—	—

tures for NH_4Br and NH_4I decrease, respectively, from 253° to 207°K, and from 232° to 216°K as the pressure is increased from zero to 1400 kg/cm² (in the NH_4Br experiments), or to 1250 Kg/cm² (in the NH_4I experiments).

The difference in the nature of the shifts in the transition temperature for NH_4Cl, on the one hand, and for NH_4Br and NH_4I, on the other hand, as is now obvious, involves the fact that a β-δ transition takes place in the former case, but a β-γ transition in the latter case. The fact that the temperature shifts in the same way on deuteration and on application of pressure indicates that this shift is related to the change in the molar volume, which is smaller in the deuterated compounds, just as it is in the compounds when subjected to homogeneous compression.

A detailed study performed recently [56] on the phase transitions of the ammonium halides under pressures up to 10^4 atm has shown that all three compounds (NH_4Cl, NH_4Br, and NH_4I) show completely analogous phase boundaries on the p-T diagram. However, the origin on the pressure axis is shifted to higher pressures in the compounds with smaller lattice parameters. Thus, for example, the temperature for the β-δ transition of NH_4Cl (a = 3.85 Å) is 243°K, while for NH_4I (a = 4.25 Å), this transition temperature requires a pressure of more than 10,000 atm, whereas the transition would take place at 150°K at zero pressure.

Pressure reduces the molar volume of a compound, and its properties approach those of a compound of smaller volume. Thus, all of the phase diagrams of the ammonium halides may be represented as modifications of one generalized diagram in which the p = 0 axis is drawn at different levels: highest of all for NH_4Cl (which has the smallest volume, which is equivalent to the presence of a high internal pressure, even when the external pressure is zero), and lowest of all for NH_4I. The p = 0 axes for ND_4Cl, ND_4Br, and ND_4I lie somewhat higher than for the corresponding hydrogen compounds (Fig. 5).*

The low-temperature transitions in the ammonium halides, which involve only the reorientation of the ammonium tetrahedra, are obviously diffusionless transformations, and can be likened to the martensitic transition.[57] This is also indicated by the fact that these transitions take place over a certain temperature range, and show hysteresis when the temperature changes in the opposite direction. The heat-capacity curves obtained in the study of these transitions [28] are very similar to those for martensitic transitions.

Unfortunately, we know of no studies in which the microscopic picture of phase formation has been studied in the ammonium-halide transitions. Such
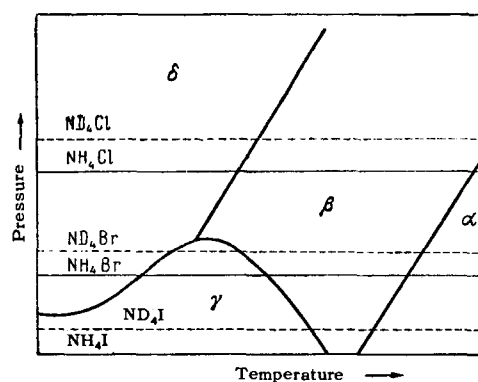
FIG. 5. Generalized phase diagram for the ammonium halides.

studies might throw more light on the problem of the nature of these transitions.

One case has been described in the literature of the shift of a phase-transition point in isotopically-substituted substances in which the transition is known to be martensitic. This is the small shift in the onset of the martensitic transition in Li^6 [36] with respect to the corresponding temperature for ordinary lithium (~93% Li^7).

III. LOW-TEMPERATURE APPARATUS FOR STUDYING THE STRUCTURES OF ISOTOPES

Most of the studies of the structures of compounds differing in isotopic composition have been carried out by ordinary x-ray methods at room temperature. In several cases, the x-ray diffraction patterns have been taken at temperatures below 0°C. These temperatures were attained by blowing over the specimen a gas which had been passed through a coil chilled to the appropriate temperature with liquid nitrogen or another cooling liquid. Studies on the isotope effects in the structural properties of the elements have been conducted, as a rule, at lower temperatures, close to absolute zero. This is due to the fact that the first attempts to discover isotope effects were made on the light elements showing the maximum relative mass difference between isotopes (hydrogen, helium); these elements are solid only at such temperatures (the solidification of helium also requires a certain definite pressure, as well as refrigeration). Low temperatures are also required in the x-ray diffraction study of the isotopes of the second inert gas after helium, i.e., neon. The need for low temperatures in studying isotope effects in the structural properties of the elements also involves the fact that the size of these effects in a number of cases increases with decreasing temperature.

The application of low-temperature methods is not the only factor rendering instrumental problems very important in the study of such objects as, e.g., the isotopes of hydrogen. Such factors also include the low scattering power of the specimens, the rapid

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*Deuteration of NH_4Cl, NH_4Br, and NH_4I is equivalent to the application of pressures of 830, 1000, and 400 atm, respectively.

decline of the intensity of the diffraction lines with scattering angle, etc.

In the x-ray diffraction studies of the hydrogen isotopes and their mixtures, the x-ray source was the fine-focus x-ray tube of B. Ya. Pines.[59,60] The advantages of this tube ensured the possibility of obtaining x-ray patterns even from such poor scatterers as the hydrogen isotopes in relatively short exposure times (2—3 hours). Schematic diagrams of cryostats for preparation and x-ray study of condensed-gas specimens (hydrogen isotopes and their mixtures, [61,80,101] neon isotopes [88]) are shown in Figs. 6a and b. One of these (Fig. 6a) is designed for taking diffraction patterns of finely-crystalline specimens, as obtained by condensation from the gas phase, and the other (Fig. 6b) for preparing and taking diffraction patterns of single-crystal and coarsely-crystalline specimens, as obtained by crystallization from a liquid phase having a high vapor pressure over the condensed phase.

beryllium specimen holder (15) is sealed. The gas being studied is condensed as the liquid in this holder, and is then crystallized by lowering the temperature in the cryostat by pumping off the vapors of the cooling liquid. In both cryostats, the evacuated space is sealed off by a cap (5, 14) having a beryllium window to admit the x-ray beam. The cassette containing the x-ray film is placed inside the cap, and serves at the same time as the liquid-nitrogen shield for the specimen.

Diagrams of the cryostats used to take x-ray diffraction patterns of the isotopes of helium [63,64,65] are shown in Figs. 7 and 8. In the cryostat of Fig. 7, which was the first one used to study solid helium,[65] x-rays from the tube F pass through the window V in the seal into the Dewar. An aluminum tube A, in which the helium has been condensed, can be turned by means of the flexible drive G, which is attached by a joint to the disk b. In order to maintain a low enough temperature in the tube containing the helium, it is placed together with the camera and the rotation mechanism in a heavy copper jacket partly submerged in liquid helium. In addition, the copper rod H and the wick E are submerged in the liquid helium. The liquid nitrogen shield is a disk soldered to tubes through which liquid air is passed.
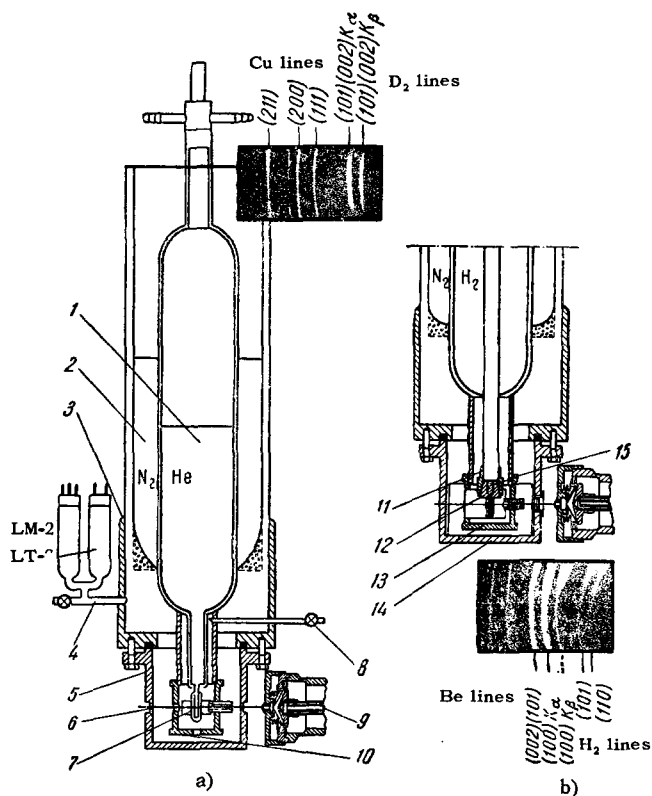
FIG. 6. Cryostats for x-ray diffraction studies of condensed gases.

FIG. 7. Cryostat for x-ray diffraction studies of solid helium.

The cryostats consist of a Dewar flask (1) for liquid helium (or hydrogen), with a liquid-nitrogen shield (2). The helium Dewar in the cryostat of Fig. 6a ends in a copper capillary (7) of diameter 1 mm. This capillary is cooled from within by liquid helium, and the gas being studied is condensed on it. In the cryostat of Fig. 6b, a copper tube passes through the Dewar; this tube ends in a ground joint to which a
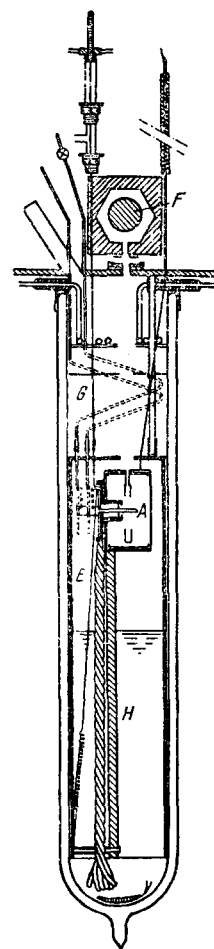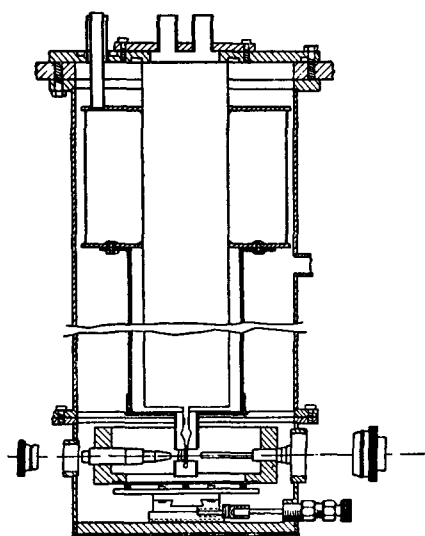
a)

FIG. 8. Cryostat for x-ray diffraction studies of solid helium.

b)

The x-ray diffraction study of the lithium isotopes was performed at various temperatures, including that of liquid hydrogen. In order to take the patterns at this temperature, the specimens were immersed in liquid hydrogen together with the x-ray film. The x rays were admitted into the glass Dewar containing the liquid hydrogen through two beryllium windows, which were foils attached with vacuum cement in the form of flat plates to the surfaces of both sides of the Dewar flask [66,67] (Fig. 9). The structures of the isotopes of hydrogen and helium have been studied not only by x-ray methods, but also by neutron diffraction. Figure 10 shows a cryostat used in neutron-diffraction studies of the hydrogen isotopes.[68,69] It does not differ in principle from the cryostat for taking x-ray
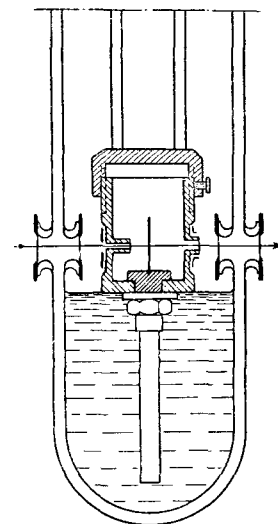
FIG. 9. Cryostat for x-ray diffraction studies of metal specimens at low temperatures.

The overall form of the cryostat used in the most recent studies [63,64] on the structures of He[4] and He[3] is shown in Fig. 8a, while Fig. 8b shows a part of this cryostat made to permit oscillation of the specimen. The helium Dewar b in this case has an annular cross-section, so that the shaft a can be inserted along its axis. One end of this shaft emerges from the cryostat through the seal, and is set into oscillation, while the beryllium specimen holder f in which the helium is condensed is pressed into its other end. Both ends of the beryllium specimen holder have cavities filled with hydrogen to serve as vapor-pressure thermometers. The pressure necessary for crystallization is applied to the helium in the specimen holder through the capillary h.

To cylinder containing the gas being studied

To forepump

To manometer

To manometer

FIG. 10. Cryostat for neutron-diffraction studies.

Neutron beam

diffraction patterns (see Fig. 6b), but has the following peculiarities:

1. Instead of the beryllium specimen holder, which is a poor absorber of x rays, here the container for the substance being studied is a cylinder made of titanium-zirconium alloy (32% titanium), which gives no coherent scattering of neutrons. This container is attached to the bottom of the reservoir containing the refrigerant by means of an indium gasket.

2. The cryostat for neutron diffraction differs from the x-ray cryostat in being of all-metal construction. It does not contain a removable cap or window for admitting neutrons. The outer casing and the liquid nitrogen screen through which the neutron beam passes are made of copper. They are separated from the specimen container by distances of 100 mm, so that the neutrons which they scatter will not enter the counter through the slit system aimed at the specimen.

In the neutron-diffraction studies of the structure of He[4], [70] an apparatus was used which had been applied earlier to study the atomic distribution in liquid helium.[71] This was an all-metal cryostat consisting of a central tube attached to the specimen container. The tube was surrounded by several concentric vessels containing liquid nitrogen and liquid helium, which were joined to the outer jacket at the top of the cryostat. The vacuum in the cryostat was maintained with a diffusion pump. The specimen container, the shield, and the outer jacket (at the level of the container) had wall thicknesses of 0.2 mm (monel), 0.01 mm (aluminum), and 0.3 mm (steel), respectively.

IV. ISOTOPIC MORPHOTROPY OF THE ISOTOPES OF HYDROGEN

The structure of the light isotope of hydrogen was discussed as early as 1913, when it was proposed on the basis of optical studies of the crystals that solid hydrogen has a cubic lattice.[72] An x-ray diffraction study of polycrystalline specimens of hydrogen was first performed in 1930 in a cryostat similar to that shown in Fig. 6a.[73] We must note, however, that the latter cryostat has several differences in construction from that used in 1930, such as to ensure better diffraction patterns, and in the final analysis, a more accurate determination of the structure of solid hydrogen. In the 1930 cryostat, the evacuated space of the Dewars was separate from the camera in which the condensation and taking of x-ray patterns were carried out. This not only made the construction of the apparatus considerably more complicated, but also gave poorer conditions for condensation. Whereas in the cryostat of Fig. 6a the excess gas was trapped on the co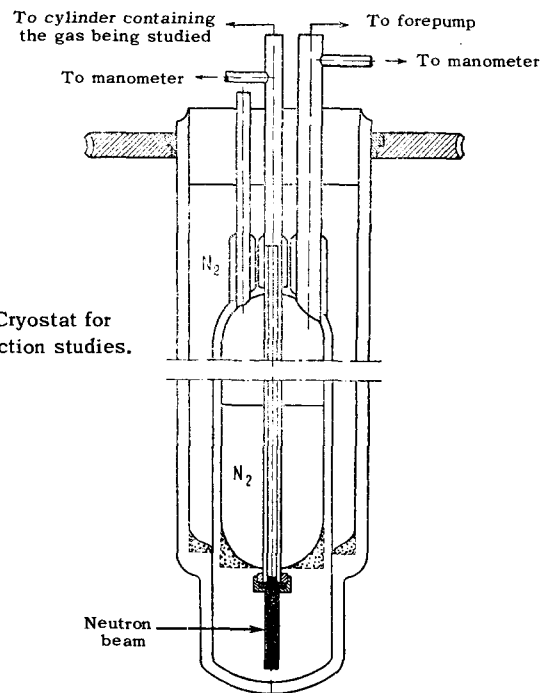ld walls of the Dewars, the condensation in the camera separate from the evacuated space of the Dewars took place in the presence of excess gas pressure, so that the gas condensed on the copper rod of 3 mm diameter in the form of a coarsely granular

layer. Thus the individual crystallites occurring in reflecting position could be separated in space, and hence, would give spots on the film displaced from the corresponding Debye-Scherrer lines. This seems to have been interpreted as indicating the presence of a larger number of powder lines than were actually present. Consequently, instead of two distinct lines at small angles, as are systematically obtained from the finely crystalline specimens in the cryostat of Fig. 6a, five lines were listed in the tables given in the 1930 study.[73] These lines were indexed on the basis of a hexagonal close-packed structure having parameters a = 3.75 kX, c = 6.12 kX, c/a = 1.633. These data on the structure of solid hydrogen found their way into the entire reference literature.

X-ray diffraction patterns were taken in the cryostat of Fig. 6a from the light and heavy isotopes of hydrogen (H_2 and D_2). Even the first photographs at 4.2°K showed differences between the diffraction patterns from specimens of protium and deuterium.[74] This made it possible to suggest that these isotopes crystallize in different structures. The observed difference could apparently not be explained as resulting from an isotopic shift in a polymorphic transition point (such as occurs, e.g., in the ammonium halides when the hydrogen is replaced by deuterium). This is excluded because the data available from the literature [79] on the temperature-dependence of the heat capacity of hydrogen permit one to assume that hydrogen shows no polymorphic transitions.

Thus, this case exhibits a new phenomenon, in which two isotopes of the same element crystallize in different crystal structures, i.e., the phenomenon of "isotopic morphotropy."

The rapid decline in intensity of the x-ray diffraction lines with increase in scattering angle is associated with the sharp angular dependences of the atomic scattering factor and the temperature factor, as are characteristic of light atoms. This decline results in an extreme sparsity in the diffraction patterns obtained from the hydrogen isotopes. The x-ray patterns of the light isotope (protium) showed only two diffraction lines at small angles; that of deuterium showed only one line. Naturally, the indexing of such diffraction patterns could not be very certain. However, if we know from independent measurements [75] the values of the density of solid hydrogen and deuterium, we can then select among the space groups of the simplest systems (cubic, hexagonal, and tetragonal) certain ones, such that the lattice parameters calculated from them agree with these density values. For example, the single diffraction line of deuterium cannot be fitted to any possible diffraction pattern from the cubic and hexagonal systems, such that the calculated parameters would give a density for deuterium equal to the literature value (0.205 g/cm³). However, this line might well be indexed as being the (101) + (002) line from a tetragonal lattice having an

axial ratio c/a = 1.73. The absence of lines at large angles, as has already been noted, can be explained by their low intensity. However, the absence of the (100) and (001) lines at small angles, as well as of the nearest line (111) at higher angles, is due to extinctions characteristic of the body-centered space group C_4^5. The parameters of the tetragonal lattice turn out here to be a = 3.35 Å, c = 5.79 Å. [61] If the unit cell contains two molecules, as is required by the space group C_4^5, the x-ray density is 0.205 g/cm³, i.e., in good agreement with the direct measurements of this quantity.

It was shown analogously that the structure of the light isotope is not cubic (this was indeed implied by the presence of birefringence in hydrogen crystals, which has since been detected [74], in contradiction to the old measurements of 1913). However, the sparsity of the diffraction pattern this time prevented a choice between hexagonal and tetragonal structures. It turned out that we can with equal justice consider the lattice of the light hydrogen isotope to be hexagonal (with space group D_{6h}^4) with an axial ratio c/a = 1.73 (a = 3.7 Å, c = 6.42 Å) or tetragonal (with space group C_4^5) with an axial ratio c/a = 0.82 (a = 4.5 Å, c = 3.68 Å). The data from a neutron-diffraction study [69] apparently favor the tetragonal structure. The results of the neutron-diffraction measurements also confirmed the x-ray data obtained previously on the structure of deuterium. The tetragonal model of the hydrogen structure is also favored by measurements of the heat capacity and nuclear magnetic resonance.

On the basis of experimental data on the anomalous heat capacity C_V, [79] Nakamura [76] has determined that, within a definite temperature range, the temperature dependence of C_V on the temperature T and the concentration ρ of ortho-hydrogen molecules may be given by the formula

$$C_V = \frac{R}{T^2} (\alpha \rho + \beta \rho^2),$$

where α = 1.1, and β = 15.7. He derived theoretically an analogous formula in which the coefficients α and β were very sensitive to the crystal structure. A calculation of these coefficients for the hexagonal [76] and tetragonal [77] structures showed that the latter gives results in better agreement with experiment.

A calculation of the possible anisotropy of the nuclear magnetic resonance for single crystals of hydrogen for the hexagonal and tetragonal structures [78] has shown that the hexagonal structure with parameters a = 3.7 Å and c = 6.42 Å [73] should exhibit an anisotropy of the second moment with respect to the six-fold axis equal to zero, but as much as 40% with respect to the two-fold axis. The tetragonal structure with parameters a = 4.5 Å and c = 3.68 Å [61] should show practically no anisotropy. Such an absence of anisotropy has been demonstrated by comparing the resonance lines from single-crystal specimens of

different orientations and from polycrystalline hydrogen. However, in addition to the evidence presented above in favor of the tetragonal structure of hydrogen, there are also experimental data contradicting this structural model. Thus, for example, the results of a study of the absorption spectra of solid parahydrogen in the infrared are better explained by assuming the hexagonal structure. [117] Apparently, the problem of the structure of the light isotope of hydrogen cannot be considered as solved yet.

The hydrogen isotopes are highly suitable objects for studying the dependence of the isotope effect in the unit-cell dimensions on the mass of the isotope. First, hydrogen has a rather large number of isotopic forms available for structural studies, and second, the relative mass difference of these isotopic forms is very large. Four of the isotopic forms of hydrogen, having molecular weights of 6, 4, 3, and 2 (i.e., T_2, [61] D_2, [61] HD, [80,62] and H_2 [61]) have been studied by x-ray diffraction methods at 4.2°K. Their relative differences $\Delta m/m_{heavy} = (m_{heavy} - m_{H_2})/m_{heavy}$ are 67%, 50%, and 33%, respectively. The structures of the light hydrogen isotope (protium) and deuterium have been discussed already. Tritium and HD turned out to be isomorphous with deuterium. The results of calculations from the x-ray patterns of these three isomorphous isotopic forms are summarized below in Table III. We see from the table that the lattice parameters of the isomorphous isotopic forms decrease with increasing molecular weight.

V. ISOTOPE EFFECTS IN THE LATTICE OF THE ISOTOPES OF THE INERT GASES (He, Ne)

X-ray diffraction patterns from solid helium were first obtained in 1938 by Keesom and Taconis. [65] The specimens of solid helium were crystallized at 1.45°K at a pressure of 35 atm in an aluminum specimen holder of diameter 2 mm and wall thickness 0.04 mm. These specimens were single crystals or coarsely crystalline blocks giving discrete reflections, even when the specimen was oscillated through 90°. These reflections could be fitted well to two Debye-Scherrer rings corresponding to interplanar spacings of 3.07 and 2.75 Å. It was shown that they could be indexed on a hexagonal close-packed structure. These data were confirmed twenty years later. Here, the specimens of solid He⁴ were crystallized in a beryllium capillary of diameter 0.125 cm and wall thickness 0.03 cm at 1.7°K at a pressure of 175 atm. [63] Several Laue patterns were obtained from the helium specimens. The [010] zone was found in a stereographic projection of the { h0l } -type reflections. Thus the orientation of the crystal with respect to the x-ray beam could be determined, and the remaining reflections were indexed. These turned out to come from planes of the types {121}, {214}, {103}, and {014} for a hexagonal lattice with an axial ratio c/a = 1.596. The

Table III. Results of calculations from the x-ray diffraction patterns of the three isomorphous isotopic forms of hydrogen: D_2, HD, and T_2.

Isotopic form	HD	D_2	T_2
sin θ	0	0.330	0.335
a	3.39	3.35	3.30
c	5.86	5.79	5.71
c/a	1.73	1.73	1.73
X-ray density at 4.2° K . . .	0.146	0.205	0.324
Literature values of density . . .	0.143 * [75]	0.205 [75]	0.32 * [81]

*Density values measured at other temperatures and extrapolated to 4.2° K.

structure of solid He^4 has also been determined by neutron diffraction[70] at 1.15°K at 66 atm, and at 1.88°K at 66 atm, with some of the specimens at 69 atm. In all cases, the neutron-diffraction patterns consisted of six lines. The positions of the lines observed in the neutron-diffraction patterns taken at 1.15°K and 66 atm agreed with a hexagonal close-packed structure with a = 3.53 ± 0.03 Å and c = 5.76 ± 0.05 Å. This structure gives a density of 0.214 ± 0.006 g/cm³.

Results were recently reported from an x-ray diffraction study of the heavy helium isotope (He^4) at 16°K and 1200 atm pressure.[64] Coarse-grained specimens were crystallized in a beryllium specimen holder (see Fig. 8a), and a sufficient number of reflections was obtained from them by oscillation over 30°. From the positions of these reflections, the interplanar spacings of several crystallographic planes were determined. These planes could be indexed well on a face-centered cubic lattice with a parameter a = 4.240 ± 0.016 Å.*

The two phases mentioned, the low-temperature hexagonal α-phase and the high-temperature β-phase, do not exhaust the list of modifications of solid He^4. Discontinuities in the velocity of ultrasound in solid helium have indicated another phase boundary in the p-T diagram of He^4 (Fig. 11a).[82] This phase boundary separates the region of existence of a new γ-phase from the α-phase. This phase occurs in the temperature-pressure range: from 1.449° ± 0.003°K and 26.18 ± 0.05 atm (the lower triple point: liquid-α solid-γ solid) to 1.778 ± 0.003°K and 30.28 ± 0.05 atm (the upper triple point: liquid-α solid-γ solid). By analogy with the modification found in the solid phase for the light helium isotope He^3 (see below), this new γ-phase has been assigned a body-centered cubic structure.

The existence of two solid modifications of the light helium isotope has been indicated by data on the volume change upon melting of He^3.[83] It was found that the curve for $\Delta V_m(p_m)$ at pressures below 141

kg/cm² has two branches. Which one is observed depends on the degree of super-cooling of the liquid at the time of freezing. A more detailed study of the p-T diagram over the temperature range 2—4.5°K revealed a slight break in the melting curve at a pressure of 141 kg/cm² and a temperature of 3.15°K, together with a solid-phase transition curve beginning at this point (Fig. 11b). The two modifications of He^3 were then studied by x-ray diffraction[84] in the same cryostats which had been used for the studies of the structure of He^4. The Laue reflections from α-He^3 (taken at 1.9°K and 100 kg/cm²) were indexed as the reflections {110}, {200}, and {121} for a body-centered cubic lattice. The powder patterns under these conditions gave only reflections corresponding to the (110) plane. The parameter of the cubic lattice of α-He^3 was determined from these reflections to be a = 4.01 ± 0.03 Å. The corresponding density was 0.154 ± 0.004 g/cm³, which was near the value 0.1515 ± 0.0002 obtained by extrapolation to the given conditions from the results of direct density measurements.[83] β-He^3 (studied at 3.3°K, 183 kg/cm²), as was shown, has a close-packed hexagonal structure. The Laue pattern showed the presence of the reflections {100}, {002}, {101}, {102}, {103}, {110}, {112}, and {201}, while reflections having h + 2k = 3n were absent for l odd. The axial lengths were determined from the powder lines for the planes (100), (002), and (101). It was found that a = 3.46 ± 0.03 Å, c = 5.60 ± 0.03 Å. The density was 0.172 ± 0.004 g/cm³. The density value extrapolated from data of direct measurements was 0.1694 ± 0.0003 g/cm³. The form of the curve for the α-β transition of He^3 on the p-T chart was analogous to that of the γ-α curve for He^4. This analogy led to the assertion that the γ-phase in He^4 is body-centered cubic (like the α-phase of He^3), although no direct studies of its structure have been carried out.*

We see by comparing Figs. 11a and 11b that the solid states of He^3 and He^4 apparently show the same

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*This modification was discovered several months later in He^3 (with a = 4.242 ± 0.016 Å) at 18.76°K, 1690 atm pressure.[116]

*It has been recently shown in experiments[118,119] with He^3-He^4 mixtures that α-He^3 actually goes over into γ-He^4 as the concentration of He^4 is increased.
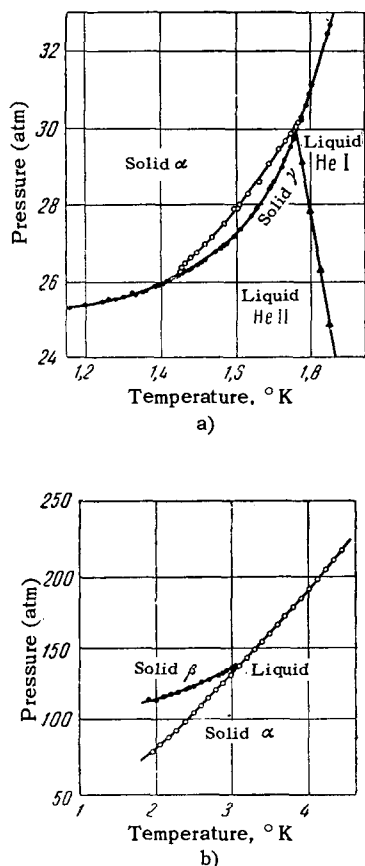
FIG. 11. Transition curves in the solid phases of He⁴ and He³.

sequence of phases, but the regions for their existence are very different in width, and considerably displaced in temperature and pressure. Thus, there are temperature regions in which the helium isotopes occur as different modifications. This morphotropy is similar to that observed in the ammonium halides or potassium acid phosphate. Just as for these compounds, the morphotropy apparently involves a shift in the polymorphic transition point, rather than the phenomenon of crystallization of each of the isotopes in its own particular structure, as occurs with protium and deuterium. Further, the possibility is not eliminated that the introduction of a second parameter, the pressure, into the picture of the hydrogen isotopes would result in each isotope (or at least one of them) exhibiting other modifications, just as for the helium isotopes.

The structure of the natural mixture of neon isotopes (~90% Ne^{20} and ~10% Ne^{22}) has been studied at 4.2°K by x-ray diffraction[85] and neutron diffraction[86] methods.

It was shown that solid neon has a face-centered cubic lattice. These studies show considerable discrepancies in the lattice parameter of neon. The x-ray data give a = 4.52 Å, while the neutron-diffraction data give 4.429 Å.

An x-ray diffraction study of the neon isotopes[88] has been performed on polycrystalline specimens

prepared by condensation from the gas phase on a copper capillary cooled from within with liquid helium (see Fig. 8a). The lattice parameters were: a_{Ne}^{20} = 4.471 ± 0.004 Å; a_{Ne}^{22} = 4.455 ± 0.004 Å.

As is predicted by theory,[87] the lattice parameter of the heavy isotope of neon is smaller than that of the light isotope. The relative difference in unit-cell volumes (1.08 ± 0.5%) was larger than that calculated from the data of the theoretical study (~0.5%).

The lattice parameter of the light isotope (a = = 4.454 Å), which should be near to that of the natural mixture, turned out to lie between the values obtained by x-ray diffraction in 1930[85] and by neutron diffraction in 1958,[86] but nearer to the latter.

We must note another peculiarity of the x-ray diffraction patterns of the light and heavy isotopes of neon. As in the case of the x-ray diffraction patterns of the hydrogen and lithium isotopes, the intensity of the diffraction lines in the pattern of the heavy isotope exceeds that of the light isotope by more than would be expected from the temperature factor values calculated by the formula

$$\frac{J_T}{J_0} = e^{-2M}, \quad \text{where} \quad M = \frac{6h^2}{mk\theta}\left(\frac{1}{4} + \frac{D(x)}{x}\right)\frac{\sin^2\theta}{\lambda^2}$$

$[D(x) = D\left(\frac{\theta}{T}\right)$ — is the Debye function].

VI. ISOTOPE EFFECTS IN THE LATTICE PARAMETERS OF ISOTOPES OF METALS (Li, Ni) AND THE TEMPERATURE-DEPENDENCE OF THESE EFFECTS

The first metal isotopes studied by x-ray diffraction methods were the lithium isotopes (Li^6 and Li^7). [89] They have a large relative mass difference $\Delta m/m = (m_7 - m_6)/m_7 \cong 15\%$, as well as simple atomic and crystal structures. This leads one to hope to find an appreciable isotope effect in the lattice parameters, and also to be able to give the obtained results a relatively simple theoretical interpretation.

Polycrystalline specimens of the lithium isotopes of diameter 0.2 mm were studied at room temperature with nickel-filtered $CuK\alpha$ radiation in a camera of diameter 114.6 mm. The exposures were 22 hours. The lines on the x-ray diffraction photographs were measured with an accuracy of 0.01 mm. The pairs of lines for (400), (411) + (330), and (420) were taken for calculation; these occurred at angles of about 61°, 69°, and 79°, respectively.

The values of the parameters calculated were: a_{Li}^6 = 3.5107 ± 0.0009 Å, a_{Li}^7 = 3.5092 ± 0.0006 Å. There is an appreciable difference between the mean values of the parameters of the isotopes (Δa = 0.0015), which seems to be quite real, although it is within the extreme limits of the parameter values possible at the given accuracy of measurement. The densities of the lithium isotopes calculated from the x-ray diffraction data are 0.462 g/cm³ and 0.539 g/cm³ for the

light and heavy isotopes, respectively. These values are close to the values 0.460 ± 0.002 g/cm^3 and 0.537 ± 0.003 g/cm^3 obtained by direct density measurements of the lithium isotopes by the flotation method and by hydrostatic weighing.[90]

Thus we may state that the lattice parameter of the light isotope exceeds that of the heavy isotope. The relative difference in atomic volumes is

$$\frac{\Delta V}{V} = 0.115\%.$$

The relative difference in lattice parameters $\Delta a/a$ of the lithium isotopes amounts to only 0.04%, while the relative mass difference $\Delta m/m$ of these isotopes is 15%. The neon isotopes (Ne^{20} and Ne^{22}), with a considerably smaller mass difference ($\Delta m/m \cong 9\%$), show a ten-fold greater difference in their parameters ($\Delta a/a \cong 0.4\%$). The reasons for such a sharp difference in the size of the isotope effect in the lattice parameters of the neon and lithium isotopes may be sought either in the differing conditions of study or in the differing nature of the binding forces in the crystals of these elements.

The differences between the conditions of study of the neon isotopes, on the one hand, and the lithium isotopes, on the other, consists in the fact that the patterns of the former were taken at 4.2°K, and the latter at 300°K. It is known from data on the temperature-dependence of the isotope effect in the lattice parameters of chemical compounds that the size of this effect can differ considerably at different temperatures. Indeed, not all chemical compounds that have been studied in this regard show an increase in this effect with decreasing temperature. Apparently, temperature-dependences of either sign can occur in the isotope effect, depending on the nature of the binding forces in the rather complex structures of the chemical compounds. Thus the problem of the temperature-dependence of the isotope effect in an element so simple in structure and nature of binding forces as lithium was all the more interesting.

The specimens of the lithium isotopes were studied by x-ray diffraction photography at 20°, 78°, and 300°K.[58] The photographs were taken in a cassette of diameter 57.3 mm. In the study at 20°K, the cassette and specimen together were completely immersed in liquid hydrogen. In the study at 78°K, the specimen was immersed halfway in liquid nitrogen. The cryostat shown in Fig. 9 was used in both cases. [66] The specimens were of 0.2 mm diameter. The specimens were 0.2 mm diameter. The x-ray diffraction photographs were measured with a comparator with an accuracy of ±0.01 mm, which ensured an accuracy of measurement of the lattice parameters of $\Delta a = \pm 0.001$ Å. As is known,[91 92] cooling of lithium below 100°K results in the appearance of a new hexagonal phase arising from a low-temperature martensitic transformation. Lines for this phase were

present on the photographs of the lithium specimens at 78° and 20°K. However, the transformation was never complete, and rather intense lines from the high-temperature body-centered cubic phase remained on the films. In order to prevent the internal stresses due to the precipitation of the new phase from affecting the results of the calculations of the isotope effect, the lattice parameters of lithium isotopes to be compared were calculated from x-ray diffraction films showing the same relative intensities of the lines of the two phases.

The calculation from the x-ray diffraction patterns of the lithium isotopes taken at different temperatures indicated that the lattice parameters of the two isotopes do not differ at room temperature within the attainable limits of accuracy. However, at low temperatures the difference in the lattice parameters of the isotopes becomes as large as $\Delta a = 0.002$ Å.*

This result was the mean obtained by comparison of the results calculated from several x-ray diffraction photographs, and apparently reflects the existence of a real isotope effect, although it is not outside the limits of the extreme values as determined by the accuracy of measurement. The curves of the temperature-dependence of the lattice parameters of the lithium isotopes are given in Fig. 12. The values of the mean linear expansion coefficients over the temperature range 78—300°K are 2.9×10^{-5} and 3.2×10^{-5} for the light and heavy isotopes, respectively. The ratio between these quantities ($\alpha_{heavy}/\alpha_{light}$)$_{78-300}$ = 1.1. It is interesting to note that this ratio is close to the value

$$\sqrt{\frac{m_{heavy}}{m_{light}}} = 1.08.$$

In spite of the fact that the isotope effect in the

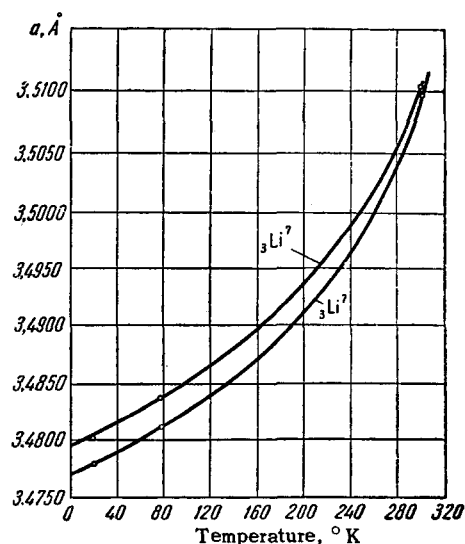FIG. 12. Temperature-dependence of the lattice parameter of the lithium isotopes.

*At 4.2° K, a_{Li^6} = 3.480 Å; a_{Li^7} = 3.478 Å.

lattice parameters of the lithium isotopes was appreciably larger at low temperatures than at room temperature, it was still considerably smaller than for the neon isotopes. This seems to provide evidence that the equal contributions to the binding forces in both isotopes made by the free electrons level out the effects due to the mass difference of the atomic nuclei in the isotopes of a metal (in this case, lithium). However, in structures with pure van der Waals binding forces, these differences are manifested especially clearly. The hypothesis that we can expect metals in general to show small values of the isotope effect in the lattice parameters, as for lithium, was tested. To do this, x-ray diffraction studies were performed on the isotopes of another metal, nickel (Ni^{58} and Ni^{64}).[93] These isotopes have a mass difference a little smaller than that of the lithium isotopes ($\Delta m/m = 9\%$, as for the neon isotopes). The specimens of the nickel isotopes were thin foils (2—3 μ thick) prepared by electroplating the metal from solutions of compounds of the pure isotopes.[94] The purity of the foils was at least 99.98%. The x-ray diffraction patterns of the specimens were taken at 78°K and at room temperature by the methods of backscattering and photography in a cylindrical cassette of diameter 114.6 mm. The patterns were taken with nickel-filtered $CuK\alpha$ radiation. The specimen-film distance and the exact value of the lattice parameter were determined from the distance between the components of the $K\alpha$ doublet of the (420) line.[95]

In the x-ray diffraction study at 78°K, liquid nitrogen was flowed over the specimen continuously during the exposure.

The results of the calculations from the x-ray diffraction patterns of the nickel isotopes obtained at 78° and 300°K permit us to conclude that:

1. The absolute magnitude of the isotope effect in the lattice parameters for the nickel isotopes is very small, even smaller than for the lithium isotopes (at 78°K, $\Delta a = 0.0005 \pm 0.0002$ Å).

2. Just as for the lithium isotopes, the isotope effect is temperature-dependent. The linear expansion coefficient over the temperature range 78—300°K is higher for the heavy isotope than for the light isotope ($\alpha_{heavy} = 9.9 \times 10^{-6}$; $\alpha_{light} = 8.8 \times 10^{-6}$), the ratio of the linear expansion coefficients being close to the mass ratio of the isotopes:

$$\frac{\alpha_{heavy}}{\alpha_{light}} = 1.12; \quad \frac{m_{heavy}}{m_{light}} = 1.10.$$

3. At room temperature the isotope effect is near to zero, but seems to be negative:

$$(\Delta a = -0.0002 \pm 0.0002 \text{ Å}).$$

VII. ATTEMPTED THEORETICAL TREATMENTS OF THE PROBLEM OF ISOTOPE EFFECTS IN THE STRUCTURAL PROPERTIES OF SOLIDS

The equilibrium distance between two neighboring particles in a crystal structure is determined in the first approximation by the position of the minimum in the curve of the potential energy of interaction between these particles.

This curve is independent of temperature and (as is usually assumed) of the atomic weight of the interacting particles. Thus, isotopic substitution of one or both interacting particles would not, at first glance, bring about a change in their relative positions. However, a particle is not at rest at the bottom of the potential well, even at absolute zero, but undergoes zero-point oscillations. If we take into account the zero-point oscillations, which are a pure quantum effect, we find that the distance between the interacting particles depends on their masses. The greater the energy of the oscillating particles, the greater the mean distance between these particles becomes, owing to the symmetry of the potential curve.[96] The frequency of the zero-point oscillations, and hence their energy, is inversely proportional to the square-root of the masses. Thus it is large for atoms of light elements. The isotopes of the light elements, which have considerable relative mass differences, have zero-point oscillation energies which are not only large in absolute terms, but also differ appreciably among themselves.

If only one of the types of atoms in a chemical compound undergoes isotopic substitution, the relative change in the reduced mass will also be largest when the isotopically substituted atoms are those of light elements, for example, in the deuteration of a hydrogen compound. According to the Debye theory, the energy of the zero-point oscillations is E_0 = (9/8) $R\theta$ (where θ is the Debye temperature). The difference in zero-point energy between two isotopes is

$$\Delta E_0 = \frac{9}{8} R\Delta\theta.$$

If the oscillations of the atoms in the crystal structure are small, $\theta \sim 1/\sqrt{m}$, and $\Delta\theta = \theta_2 - \theta_1 = \theta_1 \times$ ($\sqrt{m_1/m_2} - 1$). Hence $\Delta E_0 = (9/8) R\theta_1 (\sqrt{m_1/m_2} - 1)$, which < 0 for $m_1 < m_2$. That is, the energy is less for the heavier isotope. If the hydrogen crystal were to obey the law of simple harmonic oscillation, then with $\theta_H = 105°K$ and $\sqrt{m_D/m_H} = 1.4$, the value of $\Delta E_0 = -64$ cal/mole. However, actually the ratio of Debye temperatures of hydrogen and deuterium is not 1.4, but only 1.08, and hence

$$\Delta E_0 \cong -20 \quad \text{cal/mole.}$$

However, even such a relatively small difference in zero-point energies proves sufficient to give an appreciable difference in the molar volumes of these isotopes. Thus, when we take into account the zero-point oscillations, we conclude that the molar volume (or lattice parameter) of a heavy isotope must be smaller at absolute zero than that of a light isotope.

In order to determine the nature of the temperature-dependence of the difference in lattice parame-

ters of two isotopes, we must estimate the temperature variation of the difference in their energies (ΔE).

At the temperature T, the lattice energy per gram-mole is [97]

$$E = E_0 + 3RTD\left(\frac{\theta}{T}\right),$$

where

$$D(x) = \frac{3}{x^3} \int_0^x \frac{z^3 dz}{e^z - 1},$$

is the so-called Debye function; and

$$\Delta E = \Delta E_0 + 3RT\left[D\left(\frac{\theta_2}{T}\right) - D\left(\frac{\theta_1}{T}\right)\right],$$

where we assume as before that the oscillations are small and harmonic,

$$\theta_2 = \theta_1 \sqrt{\frac{m_1}{m_2}},$$

i.e.,

$$\Delta E = \Delta E_0 + 3RT\left[D\left(\sqrt{\frac{m_1}{m_2}}\frac{\theta_1}{T}\right) - D\left(\frac{\theta_1}{T}\right)\right].$$

However, $D(x)$ decreases monotonically with increasing x. Obviously, if $m_1 < m_2$, then

$$D\left(\sqrt{\frac{m_1}{m_2}}\frac{\theta_1}{T}\right) > D\left(\frac{\theta_1}{T}\right)$$

and

$$\Delta E_T = 3RT\left[D\left(\sqrt{\frac{m_1}{m_2}}\frac{\theta_1}{T}\right) - D\left(\frac{\theta_1}{T}\right)\right] > 0,$$

while $\Delta E_0 < 0$. Hence, if at 0°K, $\Delta E = \Delta E_0 < 0$ (i.e., E is greater for the lighter isotope than for the heavier one), the value of $|\Delta E| = |\Delta E_0| - |\Delta E_T|$ will decrease with increasing temperature.* If we heat the isotopes to the same temperature, the heavier isotope will take up more energy than the light isotope. This means that the heat capacity $C_{heavy} > C_{light}$. Experimental studies of the thermal properties of substances differing in isotopic composition have corroborated this law (see, e.g., the heat-capacity curves for Li^6 and Li^7 in Fig. 13[58] or the heat-capacity data for the compounds ZrH_2 and ZrD_2[98]).

The fact that the heat capacity of a heavy isotope is greater than that of a light isotope means, according to Grüneisen's Law, that the coefficient of thermal expansion of the heavy isotope is also larger. This also agrees with the experimental data. From the difference in energy levels, we may estimate the difference in lattice parameters from the data on the heat capacity C and the linear expansion coefficient α of the given substance:

$$\Delta a = \alpha \Delta T = \alpha \frac{\Delta E}{C}.$$

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*However, an inversion of the isotope effect, as observed at room temperature in nickel, cannot be explained within the framework of the Debye theory of solids.
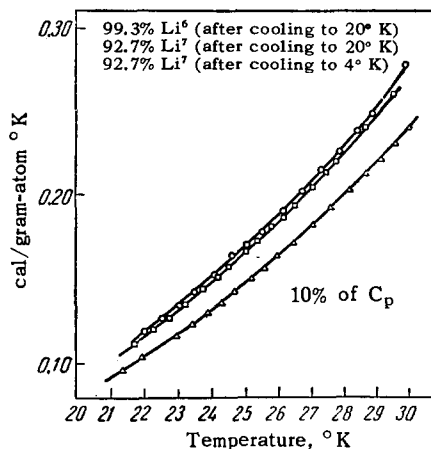

FIG. 13. Heat capacity of the lithium isotopes.

This conversion has been made for LiH,[99] but gave too low a value for Δa. Thus we must assume that the Debye theory is insufficiently accurate for this compound.

London has made a more rigorous calculation of the isotope effect in the molar volume from data on the thermodynamic properties of isotopes.[31] He wrote the free energy of the crystal structure [97]

$$F = N\varepsilon_0 + kT \sum_\alpha \ln\left(1 - e^{-\frac{h\nu_\alpha}{kT}}\right)$$

in such a form that the terms depending only on the volume were separated from those depending on the particle masses and the temperature. To do this, he subtracted from the first term (which is the interaction energy of the atoms of the crystal structure at 0°K) the part which is due to the zero-point oscillations ($\sum_\alpha \frac{1}{2}h\nu_\alpha$), and added it to the term under the summation sign to give

$$F = W_0(v) + kT \sum_\alpha \left[\frac{1}{2}\frac{h\nu_\alpha}{kT} + \ln\left(1 - e^{-\frac{h\nu_\alpha}{kT}}\right)\right],$$

where $W_0(\nu)$ is the potential energy, which is independent of the masses of the particles and the temperature.

Using known thermodynamic relations, he derived from the free energy an expression for the pressure p and the lattice energy U. In particular, $p = W_0'$ + $(\gamma/V)(U - W_0)$. The coefficient (γ/V) (where γ is the constant from Grüneisen's Law) arises here from differentiation of the frequency with respect to the volume in finding $p = -(\partial E/\partial V)_T$. By introducing the mass of the isotope M as an independent variable and assuming p to be constant, London obtained

$$\frac{M dV}{V dM} = \frac{\gamma\kappa}{V}(U - W_0 - TC_V)\frac{d\ln\nu_\alpha}{d\ln M}$$

(where κ is the compressibility).

For monatomic solids, for which

$$\frac{d \ln v_\alpha}{d \ln M} = -\frac{1}{2},$$

$$\frac{M dV}{V dM} = -\frac{\gamma \varkappa}{2V}(U - W_0 - TC_V),$$

where the difference $(U - W_0)$ is the oscillation energy in the crystal structure.

At absolute zero, $U = U_0$, while $U_0 - W_0$ is the zero-point oscillation energy $E_0 = (9/8) R\theta$. That is, at absolute zero

$$\frac{M dV}{V dM} = -\frac{9}{16}\frac{\gamma \varkappa}{V} R\theta.$$

This formula can be used to calculate the isotope effect in the molar volume in a crystal structure consisting of atoms (or molecules) of one type, i.e., a structure made of such experimentally-studied isotopes as H_2 and D_2, Ne^{20} and Ne^{22}, or Li^6 and Li^7.

For the hydrogen isotopes, the compressibility and the Grüneisen constant[32] are known: $\gamma = 2$; $\varkappa = 6 \times 10^{-4}$ cm^2/kg [$\varkappa_{H_2} = (6.8 \pm 1.5) \times 10^{-4}$ cm^2/kg, and $\varkappa_{D_2} = (4.5 \pm 2) \times 10^{-4}$ cm^2/kg]. The molar volume V of the hydrogen isotopes at $4.2°K$ is $\cong 21$ cm^3 ($V_{H_2} = 22.65$ cm^3; $V_{D_2} = 19.56$ cm^3), and the characteristic temperature $\nu \simeq 100°K$.

Thus, the relative volume change from hydrogen to deuterium ($dM/M = \frac{1}{2}$) is

$$\frac{dV}{V} = 1.3 \cdot 10^{-1}.$$

The experimental value of the change in unit-cell volume per particle is 4.8 Å^3, with a mean volume per particle in the crystal structure of 35.2 Å^3. That is, $(\Delta V/V)_{exper} = 1.4 \times 10^{-1}$, in almost exact agreement with the calculated value of the isotope effect.

Covington and Montgomery[89] measured the lattice constants of the lithium isotopes at $300°C$, and made a semiquantitative estimate of the isotope effect by a method analogous to that proposed by London. The only difference from the latter method was that they did the calculation for a single mean oscillator, rather than for an entire lattice. They obtained a value at room temperature of $\Delta a/a = 3 \times 10^{-4}$, while the experimental value is $(\Delta a/a)_{exper} = 4 \times 10^{-4}$.

London also developed his theory for the case of diatomic solids, for which, in the first approximation

$$\frac{d \ln v_\alpha}{d \ln M} = -\frac{1}{2}\frac{d \ln \mu}{d \ln M} = -\frac{1}{2}\frac{1}{1 + M/m},$$

where μ is the reduced mass ($1/\mu = 1/m + 1/M$). The formulas which he derived permitted him to calculate the isotope effect for the compounds Li^6F and Li^7F. It turned out that $\Delta a/a = 3.3 \times 10^{-4}$. The experimental value obtained from x-ray data[17] is

$$\left(\frac{\Delta a}{a}\right)_{exp} = (2 \pm 0.5) \cdot 10^{-4}.$$

The isotope effect in the lattice parameters for neon has been calculated on the basis of an estimate

of the forces acting on the atoms in the unit cell.

On the assumption that each atom of the inert gas in the crystal oscillates in the potential field of the neighboring atoms, and that the interaction potential between two atoms has the form

$$\Phi(R) = \frac{A}{R^m} - \frac{B}{R^6},$$

the energy $P(r)$ of an oscillating particle was determined[33] as a function of its displacement from the equilibrium position. The function $P(r)$ was written in series form with terms up to fourth order, which amounts to taking anharmonicity of the oscillations into account.

The discrete energy levels of an atom in the crystal structure were determined from the Schrödinger equation $\hat{H}\psi = E\psi$, where

$$\hat{H} = -\frac{\hbar^2}{2m}\Delta + P(r),$$

the energy levels are the eigenvalues E_i of the energy satisfying this equation.

If we know the eigenvalues of the energy of an atom in the crystal structure, we can write the partition function $Q = \sum_i g_i \exp(-E_i/kT)$. Hence, we can also write expressions for all the thermodynamic potentials, which can be compared with the experimental values of the macroscopic characteristics of the solid. Such a comparison will permit us to determine the parameters A, B, and m in the expression for the potential $\Phi(R)$.

In particular, it has been found for neon[34] that the best fit is given by the values: $m = 14$, $A = 0.373 \times 10^{-119}$ erg cm^{14}, $B = 0.90 \times 10^{-59}$ erg cm^6. Using these data, Johns[87] has calculated the free lattice energy of neon as a function of the interatomic distance and the temperature, as well as the equilibrium value of the lattice parameter (a_{equil}) for each temperature (from the condition $dF/da = 0$).

Since the expression for the free energy contains the mass of the interacting particles, the calculation gives different equilibrium parameters for the two isotopes. These results are given for several temperatures in Table IV.

The molar volume of Ne^{20} from the calculations exceeded that of Ne^{22} by $\sim 0.5\%$ at $0°K$, and by $\sim 0.4\%$ at $24°K$.

A comparison with the experimental data on the isotope effect in the molar volume of neon[88] shows that the calculation gives too low a value for this effect, as $(\Delta V/V)_{exper} = (1.1 \pm 0.5)\%$ at $4.2°K$.

The crystal structures of all compounds showing an anomalous isotope effect ($a_{heavy} > a_{light}$) contain hydrogen bonds joining oxygen atoms. While the ordinary van der Waals distance between two oxygen atoms is $3.4 - 3.7$ Å, a hydrogen "bridge" between them will lower this distance to $2.5 - 2.8$ Å. The compounds showing the anomalous isotope effect contain two types of hydrogen bonds: hydroxyl bonds of

Table IV.

Temperature, °K	0		12		20		24	
Isotope	Ne²⁰	Ne²²	Ne²⁰	Ne²²	Ne²⁰	Ne²²	Ne²⁰	Ne²²
a_{equil} (Å)	4.5385	4.530	4.542	4.534	4.564	4.5575	4.881	4.575

length 2.75—2.85 Å and the so-called short bonds of length 2.55 Å. In compounds containing only hydroxyl bonds (salt hydrates, pentaerythritol $C(CH_2OH)_4$, resorcinol $C_6H_4(OH)_2$, etc.), the isotope effect in the molar volume is very small, being only $(1—2) \times 10^{-4}$. In the compounds containing short bonds, the isotope effect is an order of magnitude larger, or in individual cases, two orders larger. Thus, for the compounds C_6H_5COOH, $C_2H_4(COOH)_2$, and $(CH)_2(COOH)_2$, $\Delta V/V \sim (2—3) \times 10^{-3}$; for the acid salts KH_2PO_4, KH_2AsO_4, and $NH_4H_2PO_4$, $\Delta V/V \sim (5—7) \times 10^{-3}$; while for oxalic acid dihydrate,

$$\frac{\Delta V}{V} \cong 2 \cdot 10^{-2}.$$

In a series of studies, Ubbelohde and his associates [15,35] have demonstrated the reason for the anomalous isotope effect. This is the fact that forces other than the usual van der Waals or Coulomb forces are present in crystals containing hydrogen bonds, especially the short ones. The isotope effect associated with these so-called resonance forces [36] is of sign opposite to that due to the ordinary forces. According to Ubbelohde, this is explained by the characteristics of the virtual molecular structures entering into resonance to create a new lower energy level; these virtual structures have energies closer together for hydrogen bonds than for deuterium bonds. This enhances the resonance, and hence the resonance energy level in the hydrogen compound is lower than in the deuterium compound, in contrast to the situation in crystals containing ordinary binding forces.

A simple explanation of the anomalous isotope effects can be given, even in the ordinary terms of amplitude of vibration of the hydrogen and deuterium atoms in the potential field W between the two oxygen atoms. [37,38] If the latter are situated at the points $x_0 \pm d$, then

$$W(d, x) = V(d + x_H) + V(d - x_H),$$

where $V(r)$ is the potential function of the interaction of the oxygen and hydrogen atoms. The equilibrium distance 2d between the two oxygen atoms can be found from the equation

$$\int_{-\infty}^{\infty} P(x, d, m, T) \frac{\partial V(d+x)}{\partial x} - f(d) = 0,$$

where P(x, d, m, T) is the probability function for

finding the atom of the hydrogen isotope of mass m at a given point x; $\partial V(d + x)/\partial x$ is the force acting between the hydrogen and oxygen atoms; f(d) is the force of repulsion between the oxygen atoms.

If the distribution P(m') is broader than P(m), this implies a greater probability of finding the isotope with mass m' at a point having a larger value of x. This is equivalent to a decrease in the force $\partial V/\partial x$, since at the greater distance from the oxygen atom, the attractive forces present have a potential curve of gentler slope than do the short-range repulsive forces. A decrease in the force $\partial V/\partial x$ must also decrease the force f(d), i.e., increase the equilibrium distance 2d to a value 2d'. Thus, the isotope effect can have either sign, depending on which of the isotopes (heavy or light) has a broader distribution function P(x, m). The shape of this function, in turn, depends on the total potential field U(d, x).

The interpretation given above is not the only one existing in the literature in which it is assumed that the potential field (in this case resulting from interaction between three atoms) can vary in form upon isotopic substitution. A study has recently appeared, in which it was shown that the assumption that the interatomic potential energies remain identical in isotopically-substituted liquids disagrees with a number of physical properties, and that isotopic substitution can appreciably change the depth and position of the potential function curve. [39]

Naturally, changes in the potential function can result in changes in the properties of the crystal not fitting a simple model, and hence commonly considered as anomalous.

VIII. THE MAGNITUDE AND SIGN OF THE ISOTOPE EFFECT IN CRYSTALS WITH DIFFERING BINDING FORCES

It has been shown in the previous sections that a heavy isotope in the crystal of a simple substance or compound has a lower energy, at least at low temperatures, than a light isotope. Correspondingly, the lattice parameters for the heavy isotope must be smaller than those for the light isotope. The lower energy of the heavy isotope implies that it forms stronger bonds in the structure than does the light isotope. In fact, as a rule, the work required to remove a molecule from a compound having a heavy

isotope (e.g., D_2O) and the heat of vaporization for a heavy isotope in a simple substance are larger than the corresponding quantities for a light isotope.

All these laws hold for structures with simple van der Waals binding forces (as in the isotopes of hydrogen, neon, and helium), in structures with ionic bonds (as in LiF, LiH, HfH$_2$, H$_2$Se, and H$_2$S) [Translator's comment: sic!] and in metals (Li, Ni). The sign of the isotope effect is positive ($a_{heavy} < a_{light}$) also for the solid solutions of hydrogen in metals, in the metal-like hydrides (UH$_3$, LaH$_2$), and in ammonia, water, and the ammonium halides.

For a number of the acid salts studied (KH$_2$PO$_4$, KH$_2$AsO$_4$, NH$_4$H$_2$PO$_4$, NaHCO$_3$, NaHSO$_4$), as well as for most of the organic compounds studied: C$_6$H$_4$(OH)$_2$, C (CH$_2$OH)$_4$, (COOH)$_2$·2H$_2$O, C$_6$H$_4$(COOH)$_2$, C$_6$H$_5$COOH, C$_2$H$_4$(COOH)$_2$, (CH)$_2$(COOH)$_2$, the isotope effect is of the opposite sign, $a_D > a_H$. Excluded from this type of compounds are compounds in which the hydrogen bonds involve atoms other than oxygen, e.g., nitrogen in CO(NH$_2$)$_2$ or fluorine in KHF$_2$. The isotope effect for these compounds is positive but very small.

When the isotope effect is positive, the relative difference in molar volumes in crystals differing in isotopic composition depends on the relative mass difference of the isotopes (or the difference in reduced masses in the case of compounds) and on the nature of the binding forces in the crystal.

For substances having an analogous type of binding forces, the function $\Delta V/V = f(\Delta\mu/\mu)$ is linear (Fig. 14). Here, crystals with van der Waals binding forces show the largest slope ($\Delta V/V$) ($\mu/\Delta\mu$). (According to London,[31] this slope is equal to ($\gamma\kappa/V$)Rθ for low temperatures.) This is apparently explained by their high compressibility κ, which is two orders of magnitude higher than for metals.
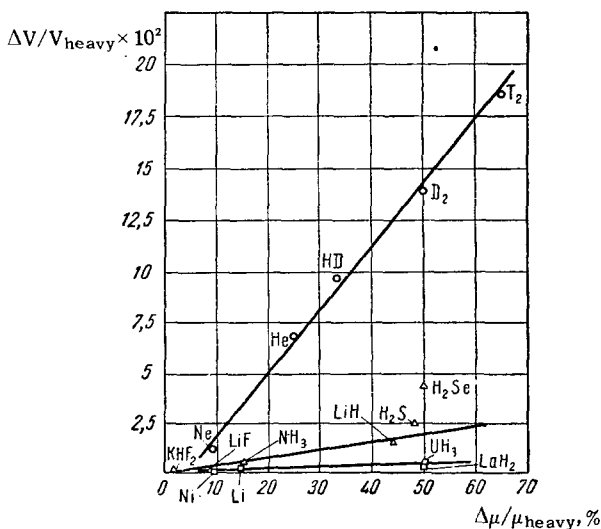
A smaller slope, and hence also a smaller isotope effect, is observed in ionic crystals and in crystals in which the hydrogen atoms do not occupy specific sites in the structure, but form part of a complex structure.* The isotope effect is even smaller for metals and the solid solutions of the hydrogen isotopes in metals.

While for $\Delta\mu/\mu = 65\%$, the value of $\Delta V/V$ for van der Waals crystals amounts to $\sim 10^{-1}$, and for ionic crystals it amounts to $\sim 2 \times 10^{-2}$, in the solid solutions of the hydrogen in metals it is only $\cong 5 \times 10^{-3}$.

Among the crystals having an anomalous (negative) isotope effect, only oxalic acid dihydrate has a large maximum value of the isotope effect in the lattice parameters. It amounts to 0.6×10^{-2} (i.e., $\Delta V/V \sim 2 \times 10^{-2}$). The other compounds having anomalous isotope effects show considerably smaller values.

IX. SOLID SOLUTIONS OF THE HYDROGEN ISOTOPES AND THE LIQUID-SOLID PHASE DIAGRAMS FOR SYSTEMS CONSISTING OF THE HYDROGEN ISOTOPES

For the overwhelming majority of solid solutions of isotopes, we can hardly expect any deviation from ideality. The differences in atomic radii of the isotopes are so small, and their properties so similar, that undoubtedly in most cases they mix to form continuous series of solid solutions having parameters linearly dependent on the concentration. Besides, even if the solid solutions of any pair of isotopes showed deviations from additivity in the lattice parameters (deviations from Vegard's Law), one could hardly detect them. This is because the change in lattice parameter produced by even a 100% substitution of one isotope by another (except among the hydrogen and helium isotopes, apparently) is near the limit of sensitivity of the modern methods of structure analysis.

Thus, if we are to study the peculiarities of solid solutions of isotopes, it is reasonable to limit the study to the solid solutions of the isotopes of hydrogen and helium. The isotopes of these elements, which differ considerably in mass, have appreciably different properties, and even crystallize (as in the case of hydrogen and deuterium) in different crystal structures. The difference in structures of hydrogen and deuterium crystals, and hence also the difference in their x-ray diffraction patterns, has made it possible to demonstrate very graphically the peculiarities of structure of the solid solutions obtained by condensation of gaseous mixtures of these isotopes.[100,101] A comparison was made of the series of x-ray diffraction patterns obtained in the cryostat of Fig. 6

FIG. 14. The size of the isotope effect in structures having differing binding forces.

*In such a case, we must, as it were, consider the mass of the oscillating particle to be that of the entire complex containing the hydrogen atoms. For example, we can assume in KHF$_2$ that the linear F–H–F groups oscillate with respect to the K atoms. In ammonia the oscillating particles are NH$_3$ groups, etc.

from H_2-D_2 solid solutions having compositions from pure hydrogen to pure deuterium, and showed that these isotopes do not form a continuous series of solid solutions. The diffraction pattern characteristic of solid hydrogen (two diffraction lines) was obtained only from specimens of mixtures in a relatively narrow concentration range near pure hydrogen. The patterns characteristic of the deuterium structure (one diffraction line) were obtained only from specimens of mixtures having a small amount of hydrogen dissolved in deuterium. The specimens of mixtures having large (near 50%) concentrations of both components gave diffraction patterns which could be explained by x-ray diffraction from both phases of a two-phase mixture. The diffraction patterns of these specimens showed three lines. Two of these coincide with the lines in the pattern of the limiting solid solution of deuterium in hydrogen, while the third coincides with the line in the diffraction pattern of the solid solution of hydrogen in deuterium.

A calculation from these patterns gave results shown in Fig. 15 in the form of graphs for both phases of V = V(c), where V is the volume per particle and c is the concentration. This calculation established more precisely the limits of solubility of hydrogen in solid deuterium and deuterium in solid hydrogen. These were 21 atomic percent and 10 atomic percent, respectively.[101]
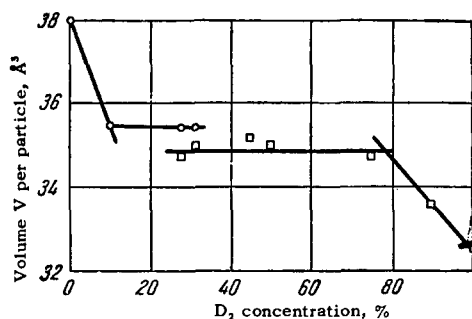

FIG. 15. Mutual solid-state solubility of hydrogen and deuterium.

The experimental data on the limited mutual solid-state solubility of hydrogen and deuterium and the existence of a concentration range in which the solid solution separates into two phases agree with the results of the theoretical studies of Prigogine et al.[102,103] and of I. M. Lifshitz and G. I. Stepanova.[104,105,106] These studies showed that, if we take into account the difference in energies of interaction of the atoms of isotopes, we must conclude that they can become correlated in arrangement in the crystal structure of a solid solution. Such a correlation will appear below a certain definite temperature (T_{cr}) depending on the relative mass difference of the isotopes ($\epsilon = \Delta m/m$) and on the Debye temperature (T_D) characterizing the binding forces in the crystal of the given element. From the estimate of I. M.

Lifshitz and G. I. Stepanova, $T_{cr} \sim \epsilon^2 T_D$. If the critical temperature is high enough that the atoms of the isotopes still have an appreciable mobility, as is necessary for separation of the solution into two phases, then the separation must take place on passing through this temperature. For hydrogen and deuterium $\epsilon = \frac{1}{2}$, while $T_D \sim 100°K$. Hence, $T_{cr} \sim 25°K$, or higher than the melting point of either solid hydrogen or solid deuterium. Thus, mixtures of these two hydrogen isotopes must separate into two phases, even in the process of crystallization from the liquid phase. However, in the direct condensation on a surface at 4.2°K (as was the case in the experiments described above), the specimens will crystallize immediately in the equilibrium form for this temperature, i.e., the mixture of the two limiting solid solutions of hydrogen in deuterium and deuterium in hydrogen, as was observed experimentally.

The phenomenon observed in the hydrogen-deuterium mixtures, in which a solid solution of the isotopes separates into two phases, can be considered in this case to result not only from correlation in the arrangement of the atoms in the structure of the solid solution, but also from the difference in the crystal structures of these isotopes.

In order to study in its pure form this phenomenon of correlation in solid solutions in isotopes, the methods described above have been used to study the problem of the mutual solid-state solubility of the isomorphous isotopic molecules HD and D_2.[107] As with the H_2-D_2 solid solutions, the D_2-HD solid solutions have a critical solution temperature (below which the separation into two phases is favored) higher than the temperatures at which the study was performed, or of the same order. (Here, $T_{cr} \sim 6°K$, while the study was performed at 4.2° and 1.5°K.) The x-ray diffraction patterns obtained can be divided into two groups:

First, the patterns from the pure isotopes and from HD-rich mixtures (up to 50 mole percent deuterium). On these patterns, the line (101) + (002) forms a sharp maximum.

Second, the patterns from mixtures rich in deuterium. On these, the line (101) + (002) is diffuse, and is distinctly doubled on microphotographs. This doubling has been ascribed to the presence in these specimens of two phases having somewhat different lattice parameters.

A calculation from the diffraction patterns gave the following results:

1) There is a broad range of solid solutions on the HD-rich side. In this range, the molecular volume gradually decreases from 69 ± 0.1 Å^3 for pure HD to 67 ± 0.1 Å^3 for the 50% solution of D_2 and HD.

2) The dependence of the lattice parameter on the composition (Fig. 16) deviates somewhat from additivity in the solid-solution range, thus indicating nonideality in these solutions.
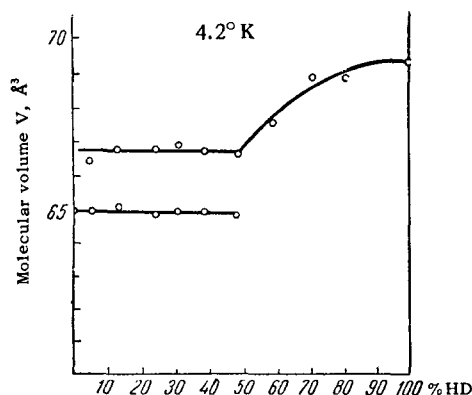
FIG. 16. Molecular volumes in the unit cells of D_2-HD solutions.

3) Mixtures in the deuterium-rich region separate into a mixture of two phases: a solid solution of composition ~50 mole percent deuterium, and a solid solution with a very small (apparently < 10 mole percent) HD content. That is, the region of phase separation is quite asymmetrically situated with respect to the concentrations of the components.

Thus, correlation in the arrangement of the isotopic atoms in solid solution sets in at low enough temperatures, not only in isotopes crystallizing in different structures, but also in isotopes forming isomorphous crystals in the solid phase; this correlation can proceed to the point of separation of the solution into two phases.

Even the pure isotopes of hydrogen consist of molecules which are not completely identical.[108] Molecules of identical electronic structure and identical nuclear masses can still differ in the orientations of the nuclear spins. Thus, hydrogen at high temperatures consists 75% of molecules having parallel nuclear spins (ortho-molecules) and 25% of molecules having antiparallel nuclear spins (para-molecules). Deuterium consists of 66% ortho-molecules and 34% para-molecules. A hydrogen molecule made of nuclei having half-integral spin obeys the Fermi-Dirac statistics, and its wave function is antisymmetric. The wave function of the hydrogen molecule can be written [109] as the product of three functions: the always-even function $R(r)$, which depends only on the relative separation of the nuclei; the function $P_J(\cos \theta)$, which can be either even or odd, depending on whether the rotational quantum number J is even or odd; and the function $S(s_1, s_2)$, which is even for parallel spins (ortho state) and odd for antiparallel spins (para state). Since the product of these three functions is the antisymmetric ψ-function, the function P_J characterizing the rotation of the molecule is even for para-molecules. Only para-molecules can have the lowest rotational quantum number J = 0, and thus they are the stable form at low temperatures. The deuterium molecule, whose nuclei have integral spin, is described by a symmetric wave function. Hence,

its function $P_J(\cos \theta)$ is even for ortho-molecules, which are thus the stable form at low temperatures. In spite of this, hydrogen and deuterium in the absence of special catalysts can remain for very long times at low temperatures as mixtures of ortho- and para-molecules. Actually, in all the structural studies of the hydrogen isotopes, the specimens were solid solutions of these molecules. If the equilibrium ratio between numbers of ortho- and para-molecules for room temperature is maintained here, the hydrogen specimens consist mainly of rotating molecules (ortho-hydrogen), while the deuterium samples consist mainly of non-rotating molecules (ortho-deuterium). However, this distinction cannot explain the difference in structures of hydrogen and deuterium. In fact, tritium, which obeys the same statistics as hydrogen, turned out to be isomorphous with deuterium, rather than hydrogen.[61] Also, direct structural studies of pure para-hydrogen and ortho-deuterium have shown that they do not differ in structure from the ortho-para mixtures of the corresponding isotopes. Apparently, the large distances between the molecules in the crystal, being much greater than the dimensions of the molecules (the intermolecular distances are 3.7—4.5 Å, while the intramolecular distance is 0.78 Å), conceal the distinction between the molecules in the ortho- and para-states.

While the pure spin modifications of the hydrogen isotopes do not result in morphotropy in the corresponding crystal structures, they can in principle show correlation effects in their solid solutions.[110] However, such effects could not be detected by x-ray methods, since ortho- and para-molecules are indistinguishable with respect to x-ray diffraction. Neutron scattering differs, as it depends also on the spin of the scattering particle, and thus distinguishes between, ortho- and para-molecules. If the arrangement of ortho- and para-molecules shows correlation, i.e., the distribution of the particles in the crystal structure is non-random, superstructure lines can appear in the neutron-diffraction pattern. Such superstructure lines have indeed been observed in the neutron-diffraction patterns of hydrogen and deuterium.[69,111] Any type of correlation, either the decomposition of a solid solution or ordering in it, must lower the entropy of the system and thus increase the heat capacity. According to a calculation by Pauling,[112] the drop in entropy associated with ordering of ortho- and para-molecules will begin at ~5°K in solid hydrogen. At a temperature of 0.001°K, according to this author, another transition will take place, consisting in the ordering of the rotational moments of the ortho-molecules. However, experimentally [79] the heat-capacity peak related to this transition was discovered later at a temperature considerably higher (1.5°K). The possibility is not excluded that the decomposition of the solid solution of ortho- and para-molecules also begins at a temperature higher than that calcu-

lated. Perhaps the heat-capacity anomaly observed in ortho-para solutions as high as 12°K [79,113] involves just such a decomposition. A study of the nuclear paramagnetic resonance of solid hydrogen has indicated that processes occur in the crystal at this temperature to increase sharply the activation energy of self-diffusion.[114] The width of the resonance lines, which reflects the rate of the diffusion processes, increases rapidly from 0.1 gauss at 14°K to several gauss at 10°K, but then remains almost constant down to 2°K.

The regions of separation of the solid solutions of the isotopes into two phases, as found at 4.2°K and below in the H_2-D_2 and D_2-HD mixtures, may either close at higher temperatures within the solid-phase region, or extend as far as the solidus line. In the former case, we should expect the liquid-solid phase diagram to be of a solid-solution type, either forming a simple loop or possessing a minimum or maximum melting point. In the latter case, more complex diagrams of the eutectic or peritectic type are possible.

In order to settle the question of the type of solid-liquid phase diagram exhibited by the hydrogen-deuterium system, heating curves were taken in a special calorimetric apparatus; mixtures of various compositions were studied over the temperature range 14—20°K. The temperature-time curves clearly showed arrests permitting the determination of the temperature at which the phase transition took place in a mixture of given concentration, and indicating the nature of this transition.

In particular, the same constant transition temperature (16.4°K) was found over a rather broad concentration range (from 26 to 52 atom percent H_2).
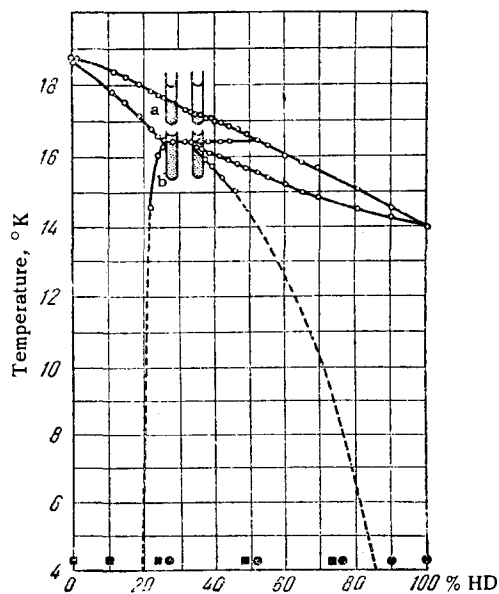

FIG. 17. Phase diagram of the H_2-D_2 system. o — Results of thermal analysis; ■, ● — results of x-ray diffraction analysis (■ — D_2 lattice, ● — H_2 lattice).

This temperature is intermediate between the melting points of the pure components, indicating peritectic melting of the mixtures. A combined study of the results of the x-ray diffraction analysis of the hydrogen-deuterium mixtures at 4.2°K and the thermal analysis over the temperature range 14—20°K made it possible to trace the general contours of the phase diagram of this system (Fig. 17). The complexity of the liquid-solid phase diagram of the hydrogen-deuterium system agrees with the considerable deviations from additivity in the densities of the liquid mixtures of these isotopes.[115]

The correctness of the proposed type of diagram has been tested visually[100] by observing the motion of the liquid-solid phase boundary.

X. CONCLUSION

We still do not know the reasons for the formation of a structure of a particular given type in the crystallization of a certain substance from the liquid or gas phase. Crystal chemistry is the science which tries to find out these reasons by comparison of the structures of particular solids with their physicochemical properties and the positions of their constituent elements in the periodic table. However, this comparison does not reveal the fundamental laws for packing of the particles of a substance in a crystal structure of a given type. The difficulty in determining these laws apparently involves the fact that they are influenced by a large set of different parameters, which differ appreciably even for neighboring elements in the periodic table. Hence, we naturally would like to consider the structures of substances differing from each other in only one known parameter, with all others being completely identical. Then the difference in structural properties could probably be explained unambiguously; this should also prove useful in determining the fundamental laws of formation of crystal structures. Examples of such substances that differ only in one parameter, the atomic weight, are the isotopes. However, it would seem at first glance that they could not differ in their structural properties. In fact, the relative positions of the particles in the crystal structure and the distances between them, or in other words, the symmetry and atomic parameters of the unit cell, depend on the magnitude and nature of the forces between the particles of which the structure is composed. Since these forces are determined by the electronic structure of the particles, they must be the same, in the first-order approximation, for isotopes of the same element. Hence, the structural properties of a substance should not change upon replacement of one of the constituent elements by an isotope. Nevertheless, it has already been known for a rather long time that replacement of hydrogen by deuterium in a number of chemical compounds results in appreciable changes in the lattice

parameters. In recent years, the study of isotope effects in the structural properties of solids has been extended to the elements and the mixtures of their isotopes. A large volume of material has already accumulated on the isotope effects in the structures and lattice parameters of compounds and elements.

This has concerned the relation of these effects to external conditions (temperature, pressure) and to the type of binding forces occurring in the crystal, as well as correlation phenomena in the arrangements of particles of isotopes in solid solutions, and the phase diagrams of systems consisting of isotopic forms of the same element.

This experimental material can serve as the basis of a new chapter of crystal chemistry, the crystal chemistry of isotopes. The very possibility of studying isotope effects in the structural properties of solids indicates that we must reconsider the definition of the concept of an isotope, which has not undergone appreciable change since Soddy introduced it originally in 1913. Isotopes not only are not "completely identical in all properties except for a small number of properties directly resulting from the atomic masses," but conversely, sometimes (as, e.g., in the case of the hydrogen isotopes) it is hard to point out a property in which they do not differ appreciably.

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