# THE ISOTOPE EFFECT IN THE MAGNITUDE OF THE UNIT-CELL VOLUMES OF NITROGEN ISOTOPES

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The lattice parameters of nitrogen isotopes are determined at 20° K. The relative change in the unit-cell volume as a function of the relative change of the nitrogen isotope masses can be described by the same linear dependence as that which holds for the isotopes of other molecular gases. The slope of the straight line for the isotopes of atomic gases (Ne and He) is apparently somewhat greater than that for molecular gases.

STUDIES of the isotope effect in the dimensions of the crystal lattices of solids began in the middle of the Thirties. At that time investigations were carried out on the isotope effects in the lattice parameters of a series of hydrogen-containing compounds upon deuteration.

Recent successes in obtaining pure isotopes and the development of methods for structure investigations have made it possible to undertake the investigation of isotope effects in the structural properties of pure elements (hydrogen[1], helium[2], neon[3], lithium[4], and nickel[5]). It turned out that the relative difference of the unit-cell volumes of two isotopes ($\Delta V/V$) is a linear function of the relative differences of their masses ($\Delta m/m$) and of the nature of the binding forces in the crystal lattice.[5]

The available experimental data have been insufficient for resolving the question of whether the points $\Delta V/V = f(\Delta m/m)$ in the case of molecular crystals ($H_2$, HD, $D_2$, $T_2$) lie on the same straight line as in the case of atomic crystals ($Ne^{20}$, $Ne^{22}$, $He^3$, $He^4$), since in the former these points are in the $\Delta m/m$ interval from 33 to 67 percent while in the latter they are in the $\Delta m/m$ interval from 10 to 25 percent. To resolve this question it was of interest to study the isotope effect in the volume of the unit cell of an element having a molecular lattice, whose isotopes have a relative mass difference less than neon ($\Delta m/m \approx 10\%$). Such an element is nitrogen ($\Delta m/m = 6.7\%$).

Three modifications of nitrogen are known. Below 35.5° K there exists $\alpha$-nitrogen (cubic[6]), in the temperature interval 35.5—63° K the $\beta$-modification is stable (hexagonal[7]), while the third, the $\gamma$-modification, exists only at low temperatures and high pressures.[8]

We have investigated the isotopes $N_2^{14}$ and $N_2^{15}$ in the $\alpha$-modification at 20° K (the light $N_2^{14}$ isotope was investigated in the form of the natural mixture: $N_2^{14}$ — 99.64 percent, $N_2^{15}$ — 0.36 percent). The light $N_2^{14}$ isotope was obtained by evaporation from the liquid phase. The heavy $N_2^{15}$ isotope was 99.2 percent pure. The nitrogen isotopes were purified from a possible oxygen impurity by passing them through heated copper filings before they entered the cryostat (see [1]).

The samples were obtained by the precipitation of the gas on a copper capillary internally cooled by liquid hydrogen.

The condensation of the residual gases of the vacuum system on the cold capillary was decreased through preliminary evacuation of the system with the aid of a sorption pump and of the cold wall of the hydrogen Dewar to $10^{-6}$ mm Hg. The photographs were taken with FeK$\alpha$ radiation obtained from a sharp-focus Pines x-ray tube with a camera 41 mm in diameter.

The x-ray photographs were measured photometrically. The distance between the lines and the effective camera diameter were determined with a precision of ± 0.02 mm.

A correction was introduced for the sample thickness and its eccentricity, the latter being determined from the standard lines of the copper capillary. The sample thickness was measured with the aid of a long-focus binocular microscope with an ocular micrometer to a precision of ± 0.02 mm. A photograph of the copper capillary with the nitrogen condensated on it taken through this microscope is shown in Fig. 1. The results of the calculations from the x-ray patterns are given in the table. Extrapolation to $\vartheta = 90°$ with the aid of the function

| Number of line | Indices | sin ϑ | | a, Å | |
|---|---|---|---|---|---|
| | | $N_2^{14}$ | $N_2^{15}$ | $N_2^{14}$ | $N_2^{15}$ |
| 1 | (220) | 0.48236 | 0.48283 | 5.681 | 5.671 |
| 2 | $\binom{221}{300}$ | 0.51209 | 0.51362 | 5.676 | 5.660 |
| 3 | (311) | 0.56646 | 0.56800 | 5.673 | 5.657 |
| 4 | (222) | 0.59041 | 0.59207 | 5.678 | 5.660 |
| 5 | (320) | 0.61594 | 0.61750 | 5.672 | 5.657 |
| 6 | (321) | 0.64057 | 0.64148 | 5.665 | 5.657 |
| 7 | (401) | 0.70545 | 0.70817 | 5.663 | 5.646 |

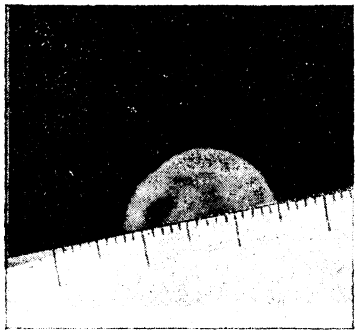

FIG. 1. Enlarged picture of the cylinder of the copper capillary with a layer of condensated nitrogen. On the scale shown in the lower portion of the figure the smallest division is 0.1 mm.

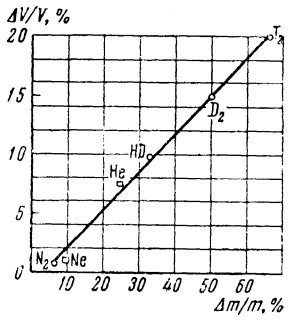


FIG. 2. The dependence $\Delta V/V = f(\Delta m/m)$ for condensated isotopes of molecular and atomic gases.

$$\frac{1}{2}\left(\frac{\cos^2\vartheta}{\sin\vartheta}+\frac{\cos^2\vartheta}{\vartheta}\right)$$

yielded the parameters

$$a(N_2^{14}) = 5.660 \pm 0.002,$$
$$a(N_2^{15}) = 5.646 \pm 0.002.$$

The relative difference in the volume $\Delta V/V = (0.74 \pm 0.2)$ percent.

The value obtained for the lattice parameter of the natural nitrogen isotope is in good agreement with the values known from the literature.

As can be seen from Fig. 2, the points ($\Delta V/V$, and $\Delta m/m$) for the nitrogen isotopes fall well on the straight line $\Delta V/V = f(\Delta m/m)$ drawn through the corresponding points of the hydrogen isotopes. Within the precision of the measurements the data for the atomic crystals of the isotopes of helium and neon fall on the same straight line. However, the average values of $\Delta V/V$ for neon and helium deviate from the straight line $\Delta V/V = f(\Delta m/m)$ for molecular crystals in different directions. This, apparently, indicates that the slope of this straight line for atomic crystals is somewhat larger than for molecular crystals.

From a comparison with the data on the isotope effect in the unit-cell volumes in metals (only data for lithium and nickel are available) it was possible to conclude that the slope of the straight line $\Delta V/V = f(\Delta m/m)$ is the larger the weaker the binding forces in the lattice. The larger slope in the case of atomic crystals indicates thus that in these crystals the binding forces in the lattice are somewhat weaker than in molecular crystals.

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298