Fizika Nizkikh Temperatur, 1996, v. 22, № 3, p. 345–347

Letters to Editor

New impurity effects in thermal expansion of $^{14}N_2$–Ar solid solutions

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Submitted November 24, 1995

Thermal expansion of solid solutions of nitrogen in argon (0.51; 2.24; 4.89% $^{14}N_2$) has been investigated in the temperature range 1–16 K. An impurity contribution $\Delta\alpha$ to a linear expansion coefficient has been separated. Negative values of $\Delta\alpha$ at $T < 4.3$ K for the solution with the nitrogen concentration 0.51 % and independence of $\Delta\alpha$ on impurity content for two concentrated solutions below 7 K have been found. A qualitative explanation of the peculiarities mentioned has been proposed.

A linear expansion coefficient of solid solutions of nitrogen in argon was investigated in the temperature range 1–16 K at nitrogen concentrations 0.51; 2.24; 4.89%. According to a phase equilibrium diagram of the system Ar–N_2 [1,2], the solutions studied are one-phase and have a fcc structure. The last fact means that linear expansion of these solutions is isotropic and described completely by one value of a linear expansion coefficient [3].

The results of the measurements in the form of a temperature dependence of the «excess» coefficients of linear expansion of the solutions Ar–$^{14}N_2$ are presented in the Fig. 1. By the «excess» coefficient $\Delta\alpha$ we mean the difference between the linear expansion coefficient of the solutions α_s and that of a matrix, i. e. $\alpha_s - \alpha_{Ar} = \Delta\alpha$.

Three peculiarities in the behavior of the «excess» linear expansion coefficient attract attention, i. e. the tendency of $\Delta\alpha$ to zero at «high» temperatures, negative values of $\Delta\alpha$ when $T < 4.3$ K for the solution Ar + 0.5% $^{14}N_2$ and independence on nitrogen concentration for the solutions Ar + 2.24% $^{14}N_2$ and Ar + 4.89% $^{14}N_2$ at low temperatures. The first of these peculiarities was observed earlier [4,5], two others were revealed experimentally for the first time.

Before discussing the peculiarities mentioned, let's describe briefly the procedure and the conditions of obtaining experimental results. Argon used contained less than 0.01% of nonisotopic impurities (impurity traces were not found by a chromatographic method). Nitrogen contained 0.002% of oxygen. The measurements were carried out using a dilatometer described previously [6]. The samples of the solid solutions were grown from a gaseous phase (without liquid one) directly in a measuring cell of the dilatometer that made it possible to avoid the occurence of a concentration gradient in the solutions [4]. Cylindrical samples were about 26 mm in height and about 22 mm in diameter. The rate of their growth was about 2 mm/h. The samples were polycrystalline with the grain dimension of the order of 1 mm. The growth of the samples and their quality were controlled visually. To reduce systematic errors in determining $\Delta\alpha$ to a minimum, we also measured the linear expansion coefficient of solid Ar. An error in determining thermal expansion of the solution and the matrix did not exceed 1.5%. The errors in the values of $\Delta\alpha$ are shown in the Fig. 1.

Now turn to the discussion of the results. In principle, both translational and rotational motions of impurity molecules contribute to the magnitude $\Delta\alpha$. The observed anomaly of the linear expansion coefficient is due to the rotational motion of impurity molecules as a contribution of the translational motion to $\Delta\alpha$ in the studied temperature and concentration ranges is negligible [5]. With the temperature increase, molecule rotation approaches a free rotation. The latter doesn't contribute to thermal expansion of the crystal ($\Delta\alpha = 0$) as the Helmholtz energy does not depend on volume for a system of free rotators. Therefore, one is to expect that at sufficiently high temperatures $\Delta\alpha$ must tend to zero. The experimental results, as seen from the Fig.1, confirm this fact. One is to assume that with the increase in noncentral forces affecting impurity molecules of nitrogen in the crystal,

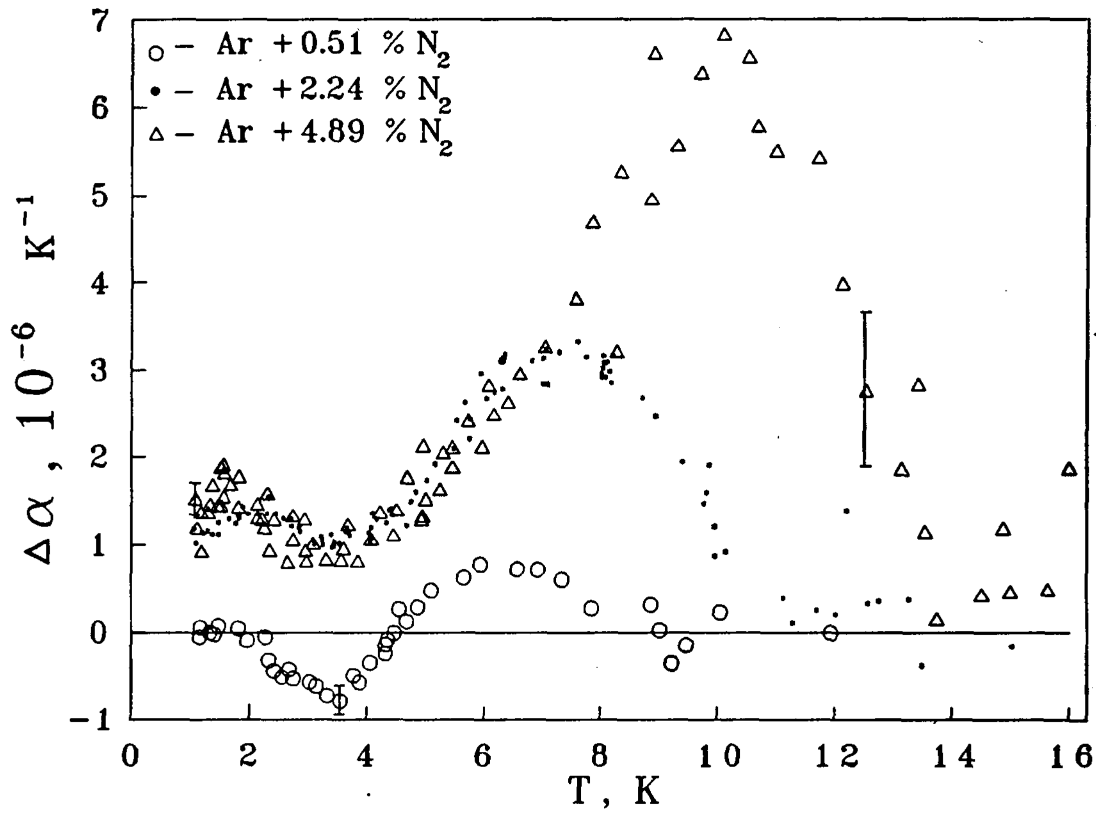

Fig. 1. Impurity contribution $\Delta\alpha$ to the linear expansion coefficient of solid solutions of nitrogen in argon.

the manifestation of the tendency $\Delta\alpha \to 0$ is displaced to the higher temperatures. It is also confirmed by the experiment (see Fig. 1), as noncentral interaction forces must increase with the growth of the nitrogen concentration.

In the solution with minimum concentration of nitrogen (0.5%), the «excess» linear expansion coefficient becomes negative below 4.3 K. This effect has to be expected from the theoretical calculations of the energy spectrum of a linear rotator in the field of octahedral symmetry. According to [7], the energy E of the first two excited states of such rotator decreases with the crystal field strengthening and, thus, with a decrease in the molar volume V. It means that the Gruneisen coefficients $\gamma = -d \ln E / d \ln V$ of these two energy levels are negative, and at sufficiently low temperatures, the effective Gruneisen coefficient is correspondingly negative. It is from a quasiharmonic approach, according to which the thermal expansion coefficient is proportional to the product of the Gruneisen coefficient times heat capacity $\gamma \cdot \Delta C$, a conclusion is drawn about the negative value of $\Delta\alpha$ for a subsystem of rotators in a crystal at low temperatures. As we know, this effect was found experimentally for the first time. No wonder that the given effect has manifested itself only in the case of the solution with the lowest nitrogen concentration, as the theoretical treatment is referred to matrix-isolated rotators (which do not interact with one another).

And, at last, let's try to explain the independence of $\Delta\alpha$ on nitrogen concentration at low temperatures in the case of two more concentrated solutions. With the increase in nitrogen concentration, the role of interaction between its molecules becomes more important. As previously shown experimentally and theoretically [8–12], at the nitrogen concentrations used (2.24 and 4.89%), indirect interaction between nitrogen molecules via deformation fields formed by them in argon lattice dominates in the solutions. Such interaction leads to the formation of orientational glass, the heat capacity of which at low temperatures depends linearly on temperature and does not depend on impurity concentration. It is seen from the Fig. 1 that $\Delta\alpha$ does not depend on nitrogen concentration. This agrees with the mentioned behavior of heat capacity in orientational subsystem (ΔC) if the Gruneisen law ($\Delta\alpha \simeq \gamma\Delta C$) for this subsystem is obeyed.

The fact that the linear dependence of $\Delta\alpha$ on temperature is not observed may be due to the temperature dependence of γ. The above mentioned qualitative explanation of the revealed peculiarities of the thermal expansion coefficient behavior $\Delta\alpha$ seems sufficiently successive, though it can not, of course, substitute for a rigorous theoretical treatment.

The authors are grateful to Yu. A. Freiman for his participation in the discussion of the results.

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