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EFFECT OF OXYGEN IMPURITY IN LOW CONCENTRATIONS ON THE HEAT CAPACITY OF SOLIDIFIED GASES

V. G. Manzhelii, Yu. A. Freiman,
G. P. Chausov, and V. V. Sumarokov

UDC 539.2

The effect of oxygen impurity on the heat capacity of simple van der Waals crystals was studied over the 1.8-15°K temperature range. In both systems under consideration there were detected appreciable anomalies in the trend of the heat capacity.

The presence of impurities in crystals can give rise to appreciable anomalies in the trend of the heat capacitance in the low-temperature range. As is well known [1], entrance into the crystal of a heavy impurity or one weakly bonded to surrounding particles causes the density of states to peak in the long-wave range of the spectrum so that the trend of the heat capacity becomes anomalous. Anomalies in the trend of the low-temperature heat capacity can be caused by other possible mechanisms too. When an impurity molecule has internal degrees of freedom, then on the density of states curve there may appear several closely spaced quasi-local plateaus. In this case a characteristic anomaly in the trend of the heat capacity ("Schottky anomaly") will appear within the range of temperatures of the order of the distance between levels.

An earlier study [2] dealt with anomalies in the trend of the heat capacity resulting from implantation of nitrogen and CO_2 molecules in crystals of inert gases, and associated with the rotational degrees of freedom of the impurity molecules.

For the purpose of determining what effect internal degrees of freedom (spin and rotational) of an oxygen molecule have on the heat capacity, the authors have studied the heat capacity of simple van der Waals crystals with oxygen impurity over the 1.8-15°K temperature range. Here we will consider the N_2–O_2 and Ar–O_2 systems.

Specimens with a uniform concentration were produced by crystallization of the substance from a gaseous jet (bypassing the liquid phase) striking a cold surface. This method of crystal growing ensured an excellent repeatability of results in an experiment with various different specimens and different ways of varying the temperature of the crystal.

The experimentally established relations for the relative change of heat capacity of Ar–O_2 and N_2–O_2 solid solutions are shown in Fig. 1. It is evident here that the magnitude

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Physicotechnical Institute of Low Temperatures, Academy of Sciences of the Ukrainian SSR, Kharkov. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 38, No. 4, pp. 603-605, April, 1980. Original article submitted September 3, 1979.

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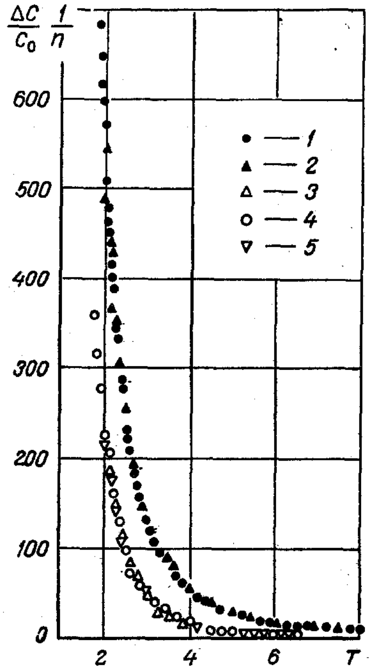

Fig. 1. Relative change of the heat capacity of the solid solutions Ar–O_2: 1) 0.98% O_2, 2) 2.02% O_2; and N_2–O_2: 3) 1.03% O_2, 4) 1.2% O_2, 5) 2.03% O_2; T, °K.

of the detected effect peaks at a temperature below 2°K. Noteworthy is the appreciable magnitude of this effect: an impurity molecule contributes over 100 times more to it than a molecule of the host substance. The effect is characterized by an approximately linear dependence on the concentration over the range of low concentrations.

The heat capacity of a solid solution can, in the case of the two systems under consideration here, be expressed as a sum of several components: $C = C_0 + C_S + C_{rot} + C_M$. Since N_2, O_2, and Ar molecules do not differ much in mass and diameter as well as in energy of intermolecular interaction, hence the last component C_M is much smaller than C_S and C_{rot} throughout the given temperature range.

At low concentrations of the oxygen impurity the contribution of the spin subsystem comes from splitting of the triplet term in the ground state $^3\Sigma_g^-$ in an oxygen molecule. The magnitude of this split is 5.62°K for a free O_2 molecule [3]. Burford and Graham, observing an anomalous trend of the heat capacity of solid N_2 and CO [4], as well as Tilford and Swenson, detecting an anomalous trend of the thermal expansivity of argon [5] when these substances contain an oxygen impurity, have found the split to be equal to 5.14°K. Simoneau subsequently studied the same systems by the method of electron-paramagnetic resonance [6]. He has shown that the split is equal to 5.3 ± 0.1°K over a wide range of oxygen concentrations (0.3-6% O_2 in N_2).

As the impurity concentration increases, not only isolated impurity molecules but also clusters of two, three, or more impurity molecules begin to contribute to the anomalous trend of thermal properties. For a cluster consisting of m O_2 molecules one can write the Hamiltonian of the spin subsystem in the form

$$H = \sum_{i=1}^{m} AS_{zi}^2 + \frac{1}{2}\sum_{i \neq k} JS_iS_k.$$

Intermolecular spin–spin interaction transforms the spectrum of the system substantially, as a result of which the anomaly in the trend of heat capacity changes in both form and range. Furthermore, interaction of impurity molecules causes the concentration dependence of this effect to depart from linearity with increasing concentration.

The authors have calculated the spectra of clusters consisting of, respectively, two and three oxygen O_2 molecules, also the contribution of these clusters to the heat capacity of a solid solution. A comparison of theoretical and experimental data pertaining to the N_2–O_2 system has made it possible to evaluate the exchange interaction constant of impurity molecules. The closest agreement between experimental and theoretical data is found when J = 2.2°K.

The combined effect of spin and rotational degrees of freedom was studied in the Ar—O_2 system. According to the graph in Fig. 1, the effect is approximately twice as large in the Ar—O_2 system as in the N_2—O_2 system over the entire given temperature range. Assuming the contributions of spin and rotational degrees of freedom to be additive, also considering that the parameters of the spin subsystem are not very sensitive to changes in the parameters of the host substance, one can separate out the contribution of the rotational subsystem and determine the barrier W which impedes rotation of an oxygen molecule in host argon. The value $W/\Theta_{rot} \sim 15$ ($\Theta_{rot} = \frac{1}{2}\hbar^2 I$) thus obtained indicates that rotational motion of O_2 molecules in host argon is strongly inhibited.

NOTATION

C, excess heat capacity of the solution above that of the host substance; C_0, heat capacity of the host substance; n, impurity concentration; T, temperature,°K; C, heat capacity of the solid solution; CS and C_{rot}, components of heat capacity due to, respectively, spin and rotational degrees of freedom in oxygen molecules; C_M, change in heat capacity due to differences in mass and in spin constants between components of the solid solution; m, number of O_2 molecules in a cluster; A, monomolecular anisotropy constant, which determines the split of the triplet term in the ground state; S, spin operator ($S = 1$); S_z, projection of the spin on the axis of the molecule; J, exchange interaction constant; W, barrier which impedes rotation of an oxygen molecule in host argon; Θ_{rot}, characteristic rotation temperature; I, moment of inertia of a molecule.

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