

We also calculated n_b under the assumption that $n = p(n_s/L)$ (Fig. 2). At reasonable values of n_b , the character of the $n_b(L)$ dependence remains unchanged, the decrease of n_b begins at the same thickness $L \sim 180 \text{ \AA}$, and only ΔL varies.

The presence of the transition is evidenced indirectly also by the $\mu(L)$ dependence. The increase of μ starting with $L \sim 200 \text{ \AA}$ is apparently due to the decrease of the scattering with decreasing concentration of the charged scatterers. Thus, from the $n_b(L)$ dependence, and also from $\mu(L)$, it follows that a semimetal-semiconductor transition occurs in Bi films at $L_t \sim 180 \text{ \AA}$. This is somewhat less than the thickness calculated theoretically from the square-well model, owing, as noted above, to the inaccuracy of the model.

An interesting feature of the $n_b(L)$ dependence is the growth of n_b when L changes from 250 to 180 \AA . A similar rise was observed in [6]. At $n_s \neq 0$, the maximum on the $n_b(L)$ curve decreases somewhat, but does not vanish (Fig. 2). It is difficult to explain satisfactorily this sharp growth of n_b at present, but it may be connected with the contribution of the surface states. For "thick" films ($L > 300 \text{ \AA}$) far from the transition point L_t , the value of the concentration n_b coincides with those given by others [6, 12].

We are grateful to V.N. Lutskii for collaboration in the experiments, to V.S. Kirichuk for help with the calculations, and to A.V. Rzhанov, A.F. Kravchenko, and V.P. Migal' for useful discussions.

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THERMODYNAMICS OF THE MELTING OF ARGON

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 ZhETF Pis. Red. 14, No. 5, 326 - 329 (5 September 1971)

We describe here the results of measurements of the volume of argon in the vicinity of the melting point in the temperature region from 197.78 to 323.15°K.

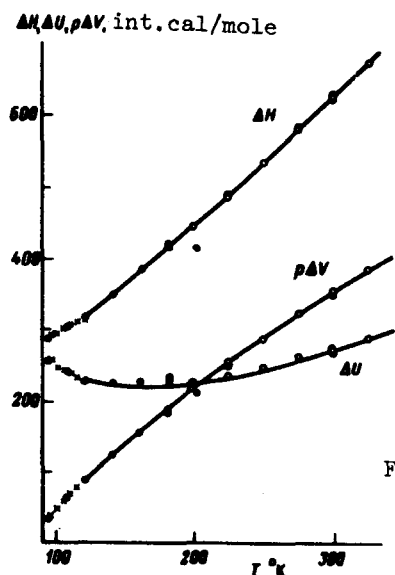


Fig. 1

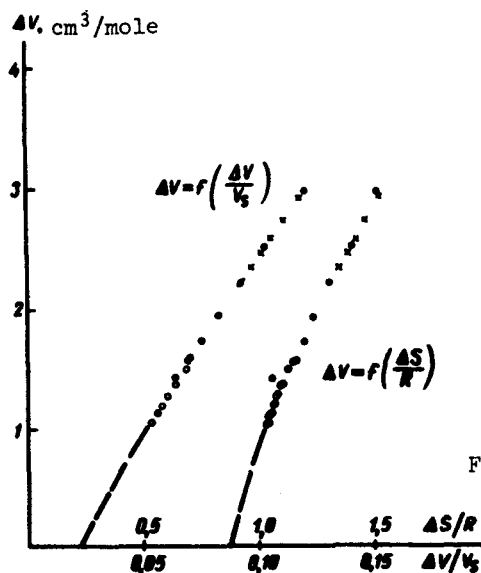


Fig. 2

Fig. 1. Dependence of the jump of the enthalpy ΔH , the jump of the internal energy ΔU , and of the work of expansion $p\Delta V$ in the melting of argon on the temperature. The following notation is used in both figures: o - our data, + - data of [3], x - data of [1], • - data of [2].

Fig. 2. Character of the relation between the volume jump ΔV , the relative volume jump $\Delta V/V_s$, and the entropy jump $\Delta S/R$.

The results of the present measurements and the data of [1 - 3] make it possible to obtain complete information on the thermodynamics of the melting of argon and to derive important relations characterizing the melting as a whole.

The measurements were made with the aid of a piston piezometer equipped with a rheostatic displacement pickup. The piezometer was filled with spectrally-pure argon at a pressure up to 2000 kg/cm². The amount of argon in the piezometer was determined by weighing. The initial volume of the piezometer was calculated using the data of [4, 5]. After filling with gas and weighing, the piezometer was placed in a chamber, in which pressure was produced by compression of gasoline. To produce the necessary temperature, the high-pressure chamber, coupled to the booster by a thin stainless-steel capillary, was immersed in a liquid thermostat. The thermostating liquid was propyl alcohol cooled where necessary with liquid nitrogen. The temperature in the thermostat was maintained constant within $\pm 0.01^\circ$. The temperature of the chamber was measured with a copper-constantan thermocouple calibrated against a standard platinum thermometer. The pressure pickup was a manganin manometer located in a separate thermostatically controlled cylinder and calibrated with an absolute weight-and-piston manometer. The pressure-measurement accuracy was ± 10 kg/cm².

As a result of the experiments and the corresponding calculations, including corrections for the deformation of the piezometer, we obtained the values of the volume of liquid and solid argon and the melting pressure of argon at each given temperature. The dependence of the melting temperature of the argon on the pressure was expressed in the form of a Simon equation, the use of which greatly simplified the problem of calculating the derivatives dT/dP . Then, on the basis of the Clausius-Clapeyron equation and other thermodynamic relations, we calculated the jumps of the enthalpy, of the internal energy, and of the entropy. The results of the measurements and calculations are given in the table and in Figs. 1 and 2. The maximum error in the measurement of the volume

T, K	$P, \text{kg/cm}^2$	$V_l, \text{cm}^3/\text{mole}$	$\Delta V, \text{cm}^3/\text{mole}$	$\Delta S/R$
197.78	6261	22.965	1.495	1.133
222.87	7947	22.328	1.364	1.106
222.61	7929	—	1.360	1.101
247.93	9734	21.815	1.261	1.084
247.77	9727	—	1.263	1.086
273.12	11604	21.305	1.183	1.074
273.00	11594	21.348	1.181	1.072
298.00	13579	20.915	1.110	1.058
298.16	13569	20.905	1.100	1.049
297.93	13573	20.882	1.114	1.062
322.83	15630	—	1.052	1.049
323.15	15657	20.460	1.050	1.047

T - melting temperature, P - melting pressure, V_l - volume of liquid phase at the melting point, ΔV - jump of volume upon melting, ΔS - jump of entropy upon melting, R - gas constant.

does not exceed $0.05 \text{ cm}^3/\text{mole}$, and the error in the jump of the volume upon melting is $0.01 \text{ cm}^3/\text{mole}$.

Proceeding to the discussion, notice should be taken of the practically complete qualitative analogy in the behavior of the thermodynamic quantities during melting of argon and sodium [6]. Just as in the case of sodium, there is a distinctive behavior of the jump ΔU of the internal energy, the temperature dependence of which has a clear-cut minimum (Fig. 1). The origin of this minimum can be easily understood by considering separately the contribution of the forces of attraction and repulsion and the increase of the total energy of the system upon melting [6].

One of the central problems in the physics of melting is that of the character of the behavior of the entropy jump ΔS and the relative volume jump $\Delta V/V_s$ with ever-increasing compression.

Let us examine Fig. 2, which shows two plots characterizing the behavior of the quantities of interest to us as functions of the volume jump ΔV . It follows quite definitely from the figure that when the volume jump ΔV decreases without limit, the relative volume jump $\Delta V/V_s$ and the entropy jump $\Delta S/R$ tend to finite values. The extrapolation leads to the following asymptotic relations

$$\left. \begin{array}{l} \frac{\Delta V}{V_s} \rightarrow 0.025 \\ \frac{\Delta S}{R} \rightarrow 0.9 \end{array} \right\} \begin{array}{l} \text{as} \\ T, p \rightarrow \infty. \end{array} \quad (1)$$

In turn, relations (1) allow us to conclude that (a) the melting curve of substances similar to argon increases continuously at all finite temperatures and pressures, i.e., the derivative dT/dp is always positive, and (b) there is no critical point of any type on the melting curve.

It should be noted that these conclusions are in full agreement with the results of "computer" experiments [7].

In conclusion, the authors thank I.N. Makarenko, V.A. Ivanov, A.F. Uvarov, and B.F. Uvarov for great help with the work.

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INTENSE FLUORESCENCE FROM THE SECOND EXCITED STATE OF MOLECULAR SOLUTIONS OF ORGANIC DYES

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ZhETF Pis. Red. 14, No. 5, 330 - 333 (5 September 1971)

According to a number of reports [1, 2], the fluorescence of molecules in solutions, which is connected with transitions from higher excited states, is very weak, owing to the rapid nonradiative energy degradation, and for its registration it is necessary to have sensitive apparatus or powerful excitation sources [3, 4]. We have observed intense short-wave emission of a number of solutions of cyanine dyes, which can be interpreted as radiation from the second excited electronic state ($S_2 \rightarrow S_0$).

The investigated solutions (dyes I - IV, see the table) have the following spectral characteristics: 1) the first electronic transition ($\lambda \sim 600 - 900$ nm, possible symmetry $'A_1 - 'B_1$) is characterized by a large oscillator strength (~ 1), the quantum yield of the fluorescent $S_1 \rightarrow S_0$ is sufficiently high for effective generation when excited by a Q-switched ruby laser [5]; 2) the absorption at the maximum of the second electronic transition ($\lambda \sim 300 - 400$ nm) is weaker by a factor of 3 - 6 than at the maximum of the first, and this transition can be characterized as fully-symmetrical $'A_1 - 'A_1$; its intensity is determined by the extent of the molecule along the symmetry axis.

The dye solutions were excited with the second harmonic (SH) of a 5-MW ruby laser and with a mercury lamp DRSh-250 ($\lambda = 313, 366, 405$ nm). The resultant fluorescence is characterized by the following regularities: when dye II is excited, two bands are observed in the fluorescence spectrum, the usual long-wave one, and a short-wave one having a large Stokes shift and a structureless contour. The short-wave fluorescence of dye II exceeds by more than one order of magnitude the fluorescence intensity of azulene from the second excited electronic state [1].

The figure shows the absorption (a) and fluorescence (b) spectra of a solution of dye II in absolute alcohol at $T = 300^\circ\text{K}$ (the solvent produced no glow whatever under these conditions).

Dye III, characterized by a larger energy gap between S_1 and S_2 than dye II, radiates only in the short-wave region when excited in the second singlet state (SH or $\lambda = 366$ nm). Dye IV, which has the largest conjugation chain and