EXPERIMENTAL INVESTIGATION OF THE HEAT CAPACITY OF THE TERNARY ALLOY Nb—Ge—Si AT LOW TEMPERATURES

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The article describes several series of measurements of the heat capacity of a massive specimen of the ternary alloy Nb—Ge—Si from 4 to 35°K containing ~8 at.% Si.

The ternary alloy Nb—Ge—Si was investigated by several authors [1, 2], and its phase diagram is known [3]. The authors of [4, 5] pointed out the possibility of increasing T_c in such an alloy. Postnikov et al. [5] discovered an increase of T_c in pellicular specimens of the alloy $Nb_3Ge_xSi_{1-x}$ with partial substitution of germanium by silicon, with change of the silicon content from 0 to 5 at.%. The largest value T_c = 20.5°K was obtained for films of $Nb_3Ge_{0.8}Si_{0.2}$ (~5% Si). The grating constant of this alloy was found to be equal to 5.150 Å, which is much less than for the alloy Nb_3Ge without Si. It was of interest to verify the possibility of increasing T_c in the same way in massive specimens upon replacement of germanium by silicon in the alloy Nb_3Ge.

We studied the temperature dependence of the heat capacity of the ternary alloy $Nb_3Ge_{0.7}Si_{0.3}$ in a massive specimen. The initial materials were single crystal Ge and Si (of semiconductor purity) and Nb with ~0.19% impurities, obtained by electron-beam melting. The specimens for the measurements were prepared by melting in a state of suspension. A molten drop was poured into a copper mold. Such a batch weighed 15 g. Chemical analysis indicated that the alloy contained ~17 at.% Ge and ~8 at.% Si. After the heat capacity had been measured, the specimens were annealed at ~750°C for 100 h. The T_c, measured by the inductive method, corresponded to 6.31°K (the measurements were carried out by O. F. Pogorelova at VNIIFTRI).

The heat capacity of $Nb_3Ge_{0.7}Si_{0.3}$ was measured by the method of the adibatic calorimeter with periodic heat supply. The process of measurement, data gathering, and processing of results was fully automated [6]. The accuracy of determining C_p was estimated to be ~0.5% at 6°K and ~0.15% at 90°K [7].

On cast specimens before annealing, four series were measured from 4.5 to ~30°K. After each series the specimen was reheated to room temperature, and before each subsequent series it was cooled to 4.2°K. After each series of measurements we found a systematic change of heat capacity. The values differed from the preceding series and considerably exceeded the limits of accuracy of measurement. For instance, at ~15°K the largest deviations in heat capacity attained 10% (between the third and fourth series). This "hysteresis" disappears at ~23-24°K, at higher temperatures the dependences $C_p(T)$ practically coincide. The nature of the dependence also changed. At ~10.4°K there appeared some excess heat capacity. Figure 1 shows these changes (curves 1-4) in coordinates $C_p/T^2(T)$. After the measurements the specimen was annealed at 750°C for 100 h. The values of $C_p(T)$ are higher than for the nonannealed specimens; with increasing temperature this difference increases (Fig. 1, curve 5). The maximum of the excess heat capacity at ~10°K shifts downward by ~0.5°K and increases. The temperature of the low-temperature superconducting transition (6.3°K) decreases by 1-1.5°K. There appears a strongly blurred excess heat capacity at ~18.3°K; this may indicate the formation of a small amount of the phase A-15 (3%) with high T_c, and the blurring is probably caused by the inhomogeneity of the specimen after annealing.

It should be pointed out that for the alloy Nb_3Ge we did not find any hysteresis of the nonannealed specimens made by the same technology (within the limits of the error of measure-

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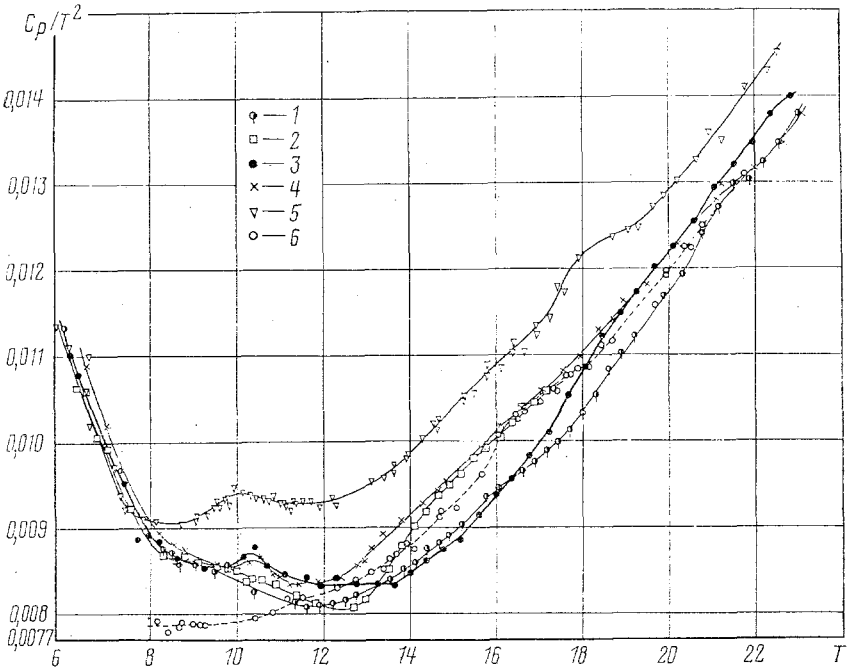

Fig. 1. Temperature-dependent changes in the heat capacity of $Nb_3Ge_{0.7}Si_{0.3}$ in coordinates $C_p/T^2(T)$ [J/kg•K³(°K)]: 1-4) for the nonannealed specimen; 5) several series on the annealed specimen; 6) for comparison the dependence for the annealed specimen of Nb_3Ge.

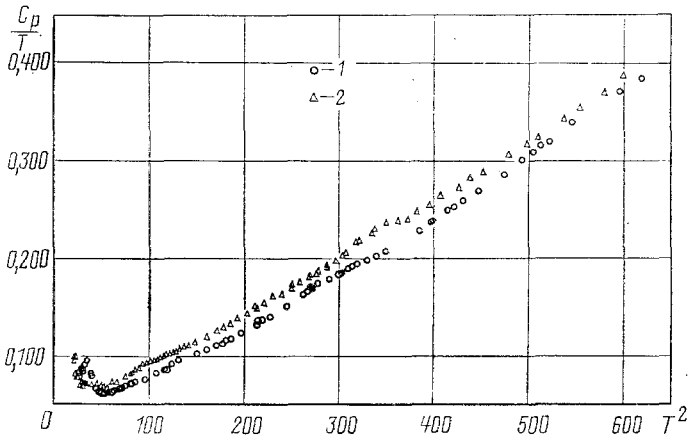

Fig. 2. Temperature dependence of the heat capacity in coordinates $C_p/T(T^2)$ [J/kg•K (K^2)]: 1, 2) specimens of Nb_3Ge and $Nb_3Ge_{0.7}Si_{0.3}$, respectively, after annealing.

ment) although the specimens were also cooled repeatedly (from 293 to 4.2°K) between series of measurements, and the temperature of the maximum of C_p of the assumed high-temperature phase of A-15 was 17°K (Fig. 1, curve 6). The ordinary dependence $C_p/T(T^2)$ for Nb_3Ge and $Nb_3Ge_{0.7}Si_{0.3}$ is shown in Fig. 2. We processed the data on heat capacity using the expression $C_p = \alpha T + bT^3 + cT^5$.

For nonannealed specimens (series 4) the following coefficients were obtained: $\alpha = 239.517 \cdot 10^{-4}$ J/kg•K², $b = 5.224 \cdot 10^{-4}$ J/kg•K⁴, $c = 5.6 \cdot 10^{-8}$ J/kg•K⁶ (for the other series the coefficients differ somewhat), the rms error of the divergence between the experimental and the calculated values is ±1%, ±2%, ±0.4% for the series 1, 3, 4, respectively. For the annealed specimens the error is ~0.4%, and the coefficients are: $\alpha = 451.809 \cdot 10^{-4}$ J/kg•K², $b = 5.044 \cdot 10^{-4}$ J/kg•K⁴, $c = 1.9 \cdot 10^{-7}$ J/kg•K⁶ for all series.

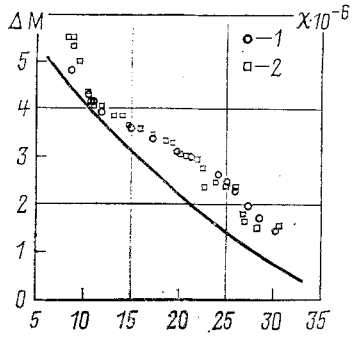

Fig. 3. Dependence ΔM(T) for nonannealed specimens (1 and 2 are the numbers of the series). For comparison we show the dependence χ(T) for a massive specimen from [10]. $\chi \cdot 10^{-6}$ cm^3/g.

In addition to measuring the heat capacity, we also carried out two series of measurements of intensity of magnetization of a specimen heated to room temperature after the first series. Figure 3 presents the dependence ΔM(T) for the temperature region 5-40°K in relative units of the indication of the mutual induction bridge [8] (the measurements were carried out by V. A. Pavlov at VNIIFTRI).

The peculiarity of the behavior of ΔM(T) at $10 < T < 24$°K is apparently connected with the more complex form of the state density than is predicted by the theory of [9], possibly also with the rearrangement of the lattice in individual inclusions of the massive specimen, and it corresponds to the irregularities of the temperature dependence of the heat capacity. The same figure also shows the dependence χ(T) [10] for a massive specimen of Nb—Ge (unfortunately, there are no literature data on measurements of the susceptibility of the ternary alloy Nb—Ge—Si), and the nature of the dependences differs.

Thus, the introduction of ~8 at.% of silicon increases T_c by ~1°K, and it probably helps stabilize the high-temperature phase at A-15.

NOTATION

Θ_D, Debye temperature; C_p, specific heat capacity at constant pressure; a, b, c, coefficients; T, temperature; T_c, temperature of superconducting transition; χ, magnetic susceptibility; ΔM, increment of magnetic moment.

LITERATURE CITED

1. E. M. Savitskii, M. I. Bychkova, and Yu. V. Efimov, "Theoretical and experimental investigations of the magnetic, electrical, and superconducting properties of solids," in: Report of the Institute of Metallurgy, Academy of Sciences of the USSR (1980), pp. 5-8.
2. V. M. Pan, O. G. Kulik, and V. I. Latyshev, "The effect of silicon on the phase composition and the critical temperature of transition to the superconducting state of niobium—germanium alloys," Fiz. Met. Metalloved., 47, No. 5, 1114-1117 (1979).
3. D. Dew-Hughes and V. D. Revlin, "Empirical relationship for the temperature T_c of some A15 superconductors," Nature, 250, No. 5469, 773-774 (1974).
4. L. S. Palatnik and I. I. Fal'ko, "Crystallochemical analysis of superconducting compounds type A_3B," Dokl. Akad. Nauk SSSR, 217, No. 3, 573-576 (1974).
5. V. S. Postnikov, V. V. Postnikov, and V. S. Zheleznyi, "On the increase of the temperature of the superconducting transition in pellicular specimens of alloys Nb—Ge doped with silicon," Fiz.-Khim. Obrab. Mater., No. 5, 172-173 (1977).
6. M. P. Orlova, Ya. A. Korolev, and L. M. Kheifetz, "Automation of the measurements of heat capacity in the interval 4.2-273°K," Zh. Fiz. Khim., 54, No. 1, 246-248 (1980).
7. M. P. Orlova and Ya. A. Korolev, "Corundum, a reference substance for low-temperature calorimetry," Zh. Fiz. Khim., 52, No. 11, 2756-2759 (1978).
8. V. A. Pavlov, V. T. Shkraba, and D. N. Astrov, "Device for measuring magnetic susceptibility," Tr. VNIIFTRI, No. 4(34), 224-228 (1973).

9. L. P. Gor'kov and O. N. Dorokhov, "On the theory of structural properties of materials with A15 lattice," Low Temp. Phys., 22, No. 1-2, 1-26 (1976).
10. V. I. Surikov, A. K. Shtol'ts, P. V. Gel'd, and L. A. Ugodnikova, "Low-temperature heat capacity and magnetic susceptibility of $Nb_{3.3}Ge_{0.7}$," Izv. Vyssh. Uchebn. Zaved., Fiz., 17, No. 5, 121-124 (1974).

HEAT CONDUCTION IN SOLIDS WITH FINITE RATE OF DIFFUSION OF HEAT AND INITIAL CONDITIONS IN THE FORM OF RANDOM FUNCTIONS

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The heat-conduction problem in solids with finite rate of diffusion of heat and initial conditions in the form of a random functions is examined. The basic probabilistic characteristics of the process are obtained.

The behavior of real distributed objects under conditions of natural, industrial, and other noise are characterized by a certain uncertainty. The description of such systems with the help of well-known deterministic approaches it not always fruitful and often does not reflect the real picture. In studying heat-transfer processes, the circumstances indicated make it necessary to solve boundary-value problems for partial differential equations with a random right-hand side, random initial conditions, and random functions in the boundary conditions.

We shall examine a homogeneous isotropic planar layer of matter with thickness l. We shall assume that there are no internal heat sources in the layer, the rate of diffusion of heat is finite, and the initial state of the layer is described with the help of random spatial functions.

In order to determine the basic probabilistic characteristics of the temperature field in the layer, it is necessary to solve the following boundary-value problem:

$$\tau_r \frac{\partial^2 T(x,\tau)}{\partial \tau^2} + \frac{\partial T(x,\tau)}{\partial \tau} = a \frac{\partial^2 T(x,\tau)}{\partial x^2}, \tag{1}$$

$$T(x,0) = \varphi_1(x), \quad \frac{\partial T(x,0)}{\partial \tau} = \varphi_2(x), \tag{2}$$

$$M_i[T(x,\tau)] \equiv \alpha_{1i} \frac{\partial T((i-1)l,\tau)}{\partial x} + \alpha_{2i} T((i-1)l,\tau) = 0, \quad i = 1, 2, \tag{3}$$

where $\alpha_{1i}\alpha_{2i} = 0$; τ_r, a, and W are the relaxation time, coefficient of thermal diffusivity, and the rate of diffusion of heat. The parameters α_{1i}, α_{2i} characterize the interaction of the layer with the surrounding medium at zero temperature. The functions $\varphi_1(x)$ and $\varphi_2(x)$ are random functions of the spatial coordinates.

Using the procedure in [1], we can write the solution of the problem (1)-(3) in the form

$$T(x,\tau) = \sum_{n=1}^{\infty} X_n(x) \int_0^l \sum_{k=1}^{2} \Phi_{kn}(t)\, \varphi_k(x)\, X_n(x)\, dx, \tag{4}$$

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