VACANCY EFFECTS IN MULTICOMPONENT ALLOYS

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A thermodynamic analysis is presented for the anomalies in the physical parameters of tool steels near the Curie point; the energy of vacancy formation is deduced from the temperature dependence of the physical parameters.

Thermodynamic analysis may be applied to various physical parameters such as the specific heat, speed of sound, elastic modulus, linear-expansion coefficient, and temperature coefficient of resistance near first-order and second-order phase transitions in deriving interesting conclusions on the probable mechanisms of these transitions. Landau has shown that the state and properties of a solid near a phase-transition point may be described in quasiparticle terms. The role of vacancies was first discussed [1,2] in relation to first-order phase transitions (melting). In the case of polymorphic transitions, one can assume that conditions arise in the initial phase as the transition temperature is approached that favor the formation of numerous quasiparticles, and the ultimate result of this is the phase transition, while intermediate results are anomalies in the physical parameters.

The thermodynamic method allows one to relate the concentration of quasiparticles in a crystalline solid to the energy of formation at the given temperature [3]:

$$c = A\exp\left\{-\frac{E}{kT}\right\}. \tag{1}$$

Then the contribution to the specific heat from the vacancies is

$$\Delta c_p = \frac{AE^2}{kT^2}\exp\left\{-\frac{E}{kT}\right\}. \tag{2}$$

If one assumes that the entire increment in the specific heat near the phase-transition point is due to the quasiparticles, then a plot of $\ln(\Delta C_p T^2)$ against $1/T$ should be a straight line, whose slope defines the energy of quasiparticle formation.

Figure 1 shows such plots of our data [4] for the specific heats of tool steels (3Kh3M-3F and 3Kh5MF1S), whose maximum error in the region of the Curie point is 0.5-1%; the observations fit closely to a straight line. The energy of quasiparticle formation E given by the slope of the line is $1.98\cdot10^{-19}$ J (1.24 eV).

A similar treatment of the linear-expansion coefficient also gives the energy of quasiparticle formation; it can be shown that the increment in the linear-expansion coefficient near the transition point due to the quasiparticles is

$$\Delta\alpha = \frac{AE}{3kT^2}\exp\left\{-\frac{E}{3kT}\right\}. \tag{3}$$

Figure 2 shows our data [5] on the linear expansion of 3Kh3M3F and 4Kh5MF1S tool steels near the Curie point as $\ln(\Delta\alpha T)^2$ plotted against $1/T$ (the maximum error in the region of the Curie point is 2-4%). Here E is $1.92\cdot10^{-19}$ J (1.2 eV) for 3Kh3M3F or $2.26\cdot10^{-19}$ J (1.4 eV) for 4Kh5MF1S.

Quasiparticles also affect the speed of sound, which is defined by

$$a_0^2 - a^2 = B\exp\left\{-\frac{E}{kT}\right\}. \tag{4}$$

The value of a_0 is obtained by straight-line extrapolation from the transition region; Fig. 3 shows our results for the region of the Curie point [6] for the same steels as $\ln(a_2^0 - a^2)$ against $1/T$ (the maximum error in the region of the Curie point was 0.35-0.5%).

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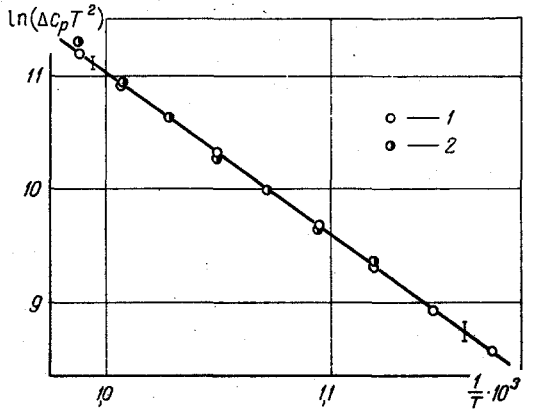

Fig. 1. Specific heats of steels: 1) 3Kh3M3F; 2) 4Kh5MF1S.

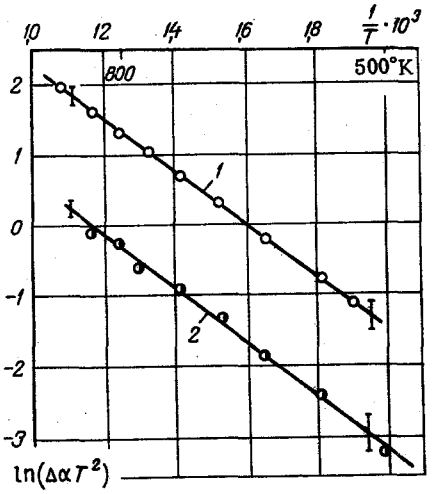

Fig. 2. Linear-expansion coefficients of steels: 1) 3Kh3M3F; 2) 4Kh5MF1S.

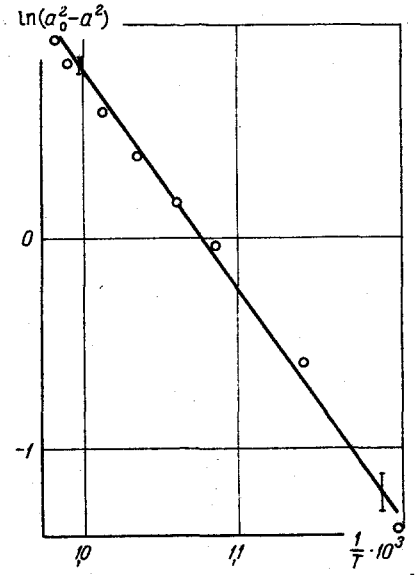

Fig. 3. Speed of sound in 3Kh3M3F steel.

Here E was $1.45 \cdot 10^{-19}$ J (0.9 eV). It is notable that these energies of formation derived from the various physical parameters are reasonably close together and reasonably similar to the energy of formation of vacancies in pure iron, $E = 2.24 \cdot 10^{-19}$ J. (There are no published data on the energies of formation of vacancies in tool steels.) This indicates that the quasiparticles formed in the transition are vacancies.

However, it must be borne in mind that other quasiparticles such as interstitial atoms may be formed in these complex multicomponent alloys; also, the above formulas deal only with the vacancy contributions, and in particular they neglect features in the thermal equation of state that may substantially influence the temperature dependence (particularly the linear expansion). A final answer to these problems requires further experiments on pure metals and on alloys.

NOTATION

c, equilibrium vacancy concentration; A, entropy factor; k, Boltzmann's constant; T, absolute temperature; E, energy of quasiparticle formation; c_p, specific heat; α, linear-expansion coefficient; a, velocity of sound; a_0, velocity of sound in absence of phase transition.

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

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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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