Heat capacity of alloys with interacting magnetic-order parameters

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The heat capacity C_p of $(Pd_xPt_{1-x})_3Fe$ alloys ordered in an fcc lattice is investigated in the temperature interval 20–300 K at a concentration phase transition from the ferromagnetic (F) state at $x = 1$ into the antiferromagnetic (AF) at $x = 0$. The concentration and temperature dependences of C_p are discussed with account taken of the experimentally reconstructed magnetic-state diagram of these alloys. It is shown that the observed singularities of $C_p(T, x)$ are due mainly to the change of the magnetic state of the alloy. The possible type of polycritical points that appear on the phase transition line with respect to the antiferromagnetic order parameter is analyzed.

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1. INTRODUCTION

Interest in theoretical as well as experimental investigations of the behavior of systems with interacting order parameters is continuously increasing (see, e.g., the review of Anisimov *et al.*[1]). These systems include apparently also alloys with mixed exchange interaction in the region of the concentration phase transition from the ferromagnetic (F) into the antiferromagnetic (AF) state. The unidirectional anisotropy observed in these systems,[2–4] as well as many other physical properties, demonstrate convincingly the important role played by the interaction between the F and AF subsystems in the onset of various kinds of singlularities in such alloy systems.

The solid solutions $(Pd_xPt_{1-x})_3Fe$ ordered in an fcc lattice of the Cu_3Au type are undoubtedly of interest for the investigation of the behavior of the heat capacity when the magnetic state changes from ferromagnetic in the alloy Pd_3Fe ($T_c = 540$ K) into antiferromagnetic in the alloy Pt_3Fe ($T_N = 164$ K). It is known [5–7] that in these solutions the palladium and platinum solutions are statistically distributed at the centers of the cubic-lattice faces, while the iron atoms occupy the vertices of the cube. Neutron-diffraction data,[5] as well as results of the investigation of the magnetic[6,7] and kinetic[7–12] properties of the alloys show that the concentration F-AF phase transition is effected in them principally in the vicinity of a certain critical concentration $x_c \sim 0.5$. The second-order phase transition lines $T_c(x)$ and $T_N(x)$ do not cross anywhere here. The fact that the electron and phonon components of the heat capacities of the alloys in questions remain practically unchanged with changing concentration[13] allows us to conclude that all the singularities of $C_p(T, x)$ are connected with its magnetic contribution C_m.

We have measured the heat capacities of $(Pd_xPt_{1-x})_3Fe$ alloys with concentrations $x = 0, 0.16, 0.31, 0.47, 0.49, 0.53, 0.57$ and 0.62, which were previously investigated[13] at temperatures lower than 20 K. The measurements were made by the adiabatic-calorimeter method in the temperature interval from 20 to 300 K. The error in the measurement of the absolute values of C_p is less than 1.5%. The method used to prepare and heat-treat the investigated alloys is described in Ref. 7.

2. EXPERIMENTAL RESULTS

The temperature dependences of the heat capacity at constant pressure $C_p(T)$ are shown in Fig. 1. It can be seen that for the AF alloy Pt_3Fe the $C_p(T)$ dependence is similar to that obtained earlier.[14] The heat capacity of this alloy has near the Néel temperature the anomaly typical of a second-order phase transition, with a peak of insignificant size. A similar anomaly is distinctly observed in all AF alloys $(Pd_xPt_{1-x})_3Fe$. When the palladium concentration increases all the way to x_c, the anomaly in the vicinity of T_N

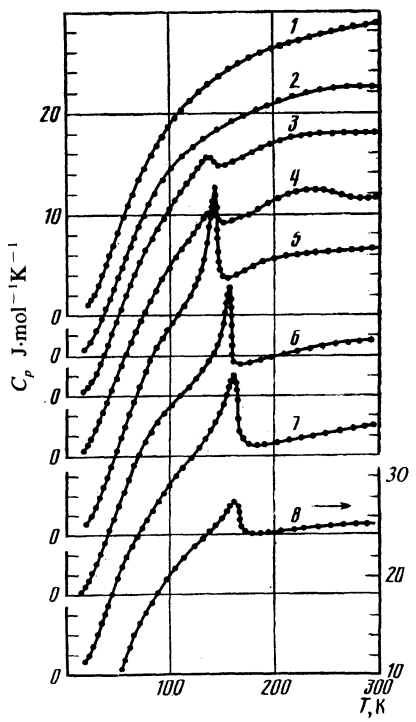

FIG. 1. Heat capacity of the alloys $(Pd_xPt_{1-x})_3Fe$ vs temperature. Curve 1 corresponds to $x = 0.62$; 2—0.57; 3—0.53; 4—0.49; 5—0.47; 6—0.31; 7—0.16; 8—0.

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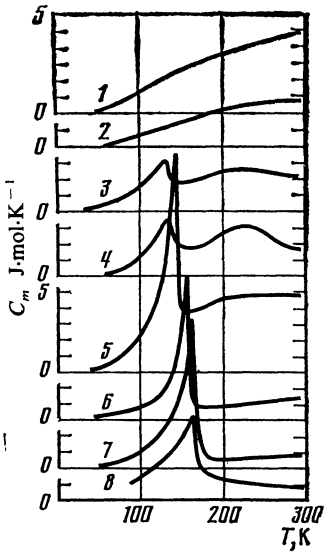

FIG. 2. Magnetic component of the heat capacity of $(Pd_xPt_{1-x})_3Fe$ alloys vs temperature. Curve 1 corresponds to $x = 0.62$; 2—0.57; 3—0.53; 4—0.49; 5—0.47; 6—0.31; 7—0.16; 8—0.

increases. The peak of $C_p(T)$ then becomes asymmetric. In alloys with $x > x_c$, however, this heat-capacity anomaly begins to decrease, and vanishes at $x \geqslant 0.6$. For alloys with $x = 0.47$ and higher, a second highly smeared anomaly appears on the $C_p(T)$ plot at temperatures $T > T_N$. According to Refs. 5 and 6 it is due to the vanishing of the long-range ferromagnetic order in the alloys.

The indicated singularities of the behavior of the heat capacity are seen most clearly on the temperature dependences of its magnetic component, which are shown in Fig. 2. The $C_m(T)$ dependences were obtained as the differences between the total and lattice heat capacities. The latter was estimated in the Debye approximation. The Debye temperatures were determined earlier[13] from measurements of the heat capacity in the temperature interval 3–20 K. Account was taken here of the conclusions of the preceding paper[13] that the electronic contribution to the heat capacities of the investigated alloys is practically independent of the palladium concentration. The other components of the heat capacity were not considered in view of their smallness in the investigated temperature region.

A comparison of the measured heat capacities of the $(Pd_xPt_{1-x})_3Fe$ alloys with the behavior of their temperature coefficients of resistivity (TCR)[7,11] shows that the main singularities of the temperature dependences of C_m and of the TCR of alloys correlate well with one another in the intermediate concentration range. In alloys in which the palladium concentration is in the vicinity of x_c, both considered properties have, besides the characteristic peak at T_N, smeared anomalies at higher temperatures, due to the F ordering. It is impossible, unfortunately, to observe the singularities of $C_m(T)$ near the Curie points of ferromagnetic alloys with $x > x_c$, since the corresponding T_c lie above 300 K.

Figure 3 shows the concentration dependences of C_m and of the TCR, obtained at 300 K. It can be seen that both characteristics behave identically with increasing palladium

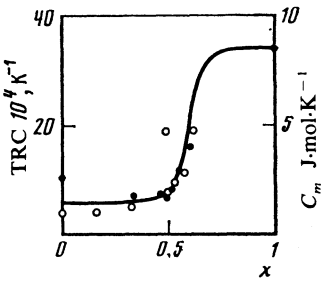

FIG. 3. Magnetic component of the heat capacity (light circles) and of the TRC (dark circles) of $(Pd_xPt_{1-x})_3Fe$ alloys vs the palladium concentration at $T = 300$ K.

concentration. At $x_c \sim 0.5$ the magnetic contribution to the heat capacity and to the TCR increases rapidly.

3. DISCUSSION OF RESULTS

The obtained $C_m(T, x)$ dependences allow us to trace the change of the magnetic state of a $(Pd_xPt_{1-x})_3Fe$ alloy during the concentration F-AF transition. An analysis of the behavior of $C_m(T)$ near the temperature phase-transition points makes it possible to identify their type. The point is that the presence of interacting order parameters leads to a substantial change in the character of the phase transitions. In particular, singular polycrytical points with their characteristic singularities can appear on the second-order transition line.

For a more detailed analysis of this question we consider the behavior of the magnetic contribution to the heat capacity near T_N. As shown in Refs. 5–9, 14, and 15, a second-order phase transition takes place at the Néel point in the Pt_3Fe alloy. In the vicinity of T_N the temperature dependences of the investigated properties are satisfactorily described in the Landau approximation. In $C_m(T)$ and the TCR, however, it is impossible to separate the fluctuation contribution. This is apparently due to the presence in the Pt_3Fe alloy of ordering-domain walls, or to the deviation of the alloy composition from stoichiometry.[14,15]

According to the model of the F-AF concentration phase transition in $(Pd_xPt_{1-x})_3Fe$ alloys,[6,7] nuclei of a ferromagnetic phase appear in the AF matrix with increasing palladium concentration. When the concentration x increases, both the number of nuclei and their average sizes increase. Neutron-diffraction,[5] magnetic, and other[6–11] investigations have shown that the F-AF concentration phase transition takes place in the alloys considered mainly in the vicinity of $x_c \sim 0.5$. Near the concentration x_c, at a temperature $T < T_N$, the F and AF systems coexist. As seen from Fig. 2 and follows from Refs. 7 and 11, in alloys with palladium concentration $0.47 < x < 0.6$, two anomalies are actually observed on the temperature dependences of C_m and of the TCR and are connected with transitions in these magnetic subsystems.

It is concluded in Ref. 6 on the basis of the results of an experimental investigation of the physical properties of $(Pd_xPt_{1-x})_3Fe$ alloys that at temperatures $T > T_N$ the concentration $x_c \sim 0.5$ is the threshold for the ferromagnet-par-

amagnet concentration phase transition. So high a threshold concentration in the considered fcc alloys is attributed in Ref. 6 to realization of correlated percolation, which was theoretically investigated in Ref. 16. The experimentally obtained concentration dependence of C_m and the TCR at $T > T_N$ (see Fig. 3) confirms this conclusion.

The observed singularities of the behavior of C_m and of the TCR at $T > T_N$ of $(Pd_xPt_{1-x})_3Fe$ alloys in the intermediate concentration region can apparently be understood only if account is taken of the interaction between the F and AF subsystems. In analogy with Refs. 1 and 17, the influence of the F subsystem of alloys on the AF subsystem will be taken into account in terms of the generalized thermodynamic field q. With increasing palladium concentration, the field q in the alloy then becomes stronger, i.e., the effect of the F subsystem on the phase transition at T_N becomes stronger. Near the critical concentration x_c this field reaches a certain value q_0 at which a polycritical point appears on the line of second-order phase transitions with respect to the AF order parameter. Since the relation $T_c > T_N$ holds for the magnetic-ordering temperatures in the interacting subsystems of the investigated alloys, this polycritical point should, according to Ref. 1, be tricritical. In alloys with concentration $x > x_c$, the phase transition with respect to the AF order parameter is already of first order. It is clear therefore that the change of the anomalies of C_m and the TCR observed in the vicinity of T_N with increasing palladium concentration is due to the position of the investigated alloy on the $T_N(x)$ line relative to the tricritical point.

It must be noted that in Ref. 12 they investigated the influence of external hydrostatic pressure on the behavior of the TCR anomaly near T_N for alloys with concentration close to x_c. It was shown there that when the external pressure is increased the Néel point shifts towards higher temperatures and the magnitude of the TCR anomaly decreases. These experimental results are attributed in Ref. 12 to the fact that in the transition-concentration-region alloys the AF subsystem is acted upon by a certain internal negative pressure due to the interaction between the F and AF subsystems. In this case the external pressure offsets part of the internal pressure and by the same token shifts the T_N of the alloy along the phase transition line towards the Néel point of the unperturbed state in the Pt_3Fe alloy. It can be seen that the introduction of an internal pressure in Ref. 12 is essentially analogous to allowance for the influence of the thermodynamic field on the character of the second-order phase transition in Refs. 1 and 17.

A careful examination of the temperature dependences of C_m shows that in alloys $(Pd_xPt_{1-x})_3Fe$ of the transition concentration region the singularity of the heat capacity near the Néel point does not follow a power law exactly. In alloys with concentration $x > x_c$ the $C_m(T)$ curves have strongly smeared anomalies in the vicinity of T_N. It is therefore difficult here even to speak of any dependence on $\tau = (T - T_N)/T_N$. In alloys with $x < x_c$, however at temperatures $T < T_N$, one can separate an interval $3\times10^{-2} < |\tau| < 3\times10^{-1}$ in which the following relation is approximately satisfied

$$C_m = A|\tau|^{-\alpha}. \quad (1)$$

A computer reduction of the experimental results by least squares, with variation of T_N and assuming the power-law dependence (1) for $C_m(\tau)$, yields for an alloy with $x = 0.47$, in the indicated interval, an exponent $\alpha = 0.58 \mp 0.04$ with a fiducial probability 0.95. As seen from Fig. 4, the region where a power law with this exponent α holds decreases with increasing difference between the alloy concentration and x_c. This probably the explanation for the change of the anomaly of C_m near T_N with changing palladium concentration. Allowance for the logarithmic increment to the heat capacity, on the basis of the equations of the fluctuation theory,[1,17] causes the value of α in the considered τ interval to decrease and to come close to the value $\alpha = 0.5$ typical of the tricritical point in the Landau approximation.

It can be seen from Fig. 4 that in the immediate vicinity of T_N the dependence of the heat capacity on τ becomes weaker. At $|\tau| < 3\times10^{-2}$ Eq. (1) holds for transition-concentration-region alloys, but with an exponent $\alpha \to 0$. The possibility of this change of the exponent α observed in the investigated alloys, as a function of the interval τ, is predicted theoretically in Refs. 1 and 17.

The experimental results show that in $(Pd_xPt_{1-x})_3Fe$ alloys with concentration $x < x_c$ the heat capacity at temperature higher than T_N decreases almost jumpwise to its minimum value. It is difficult to check on the validity of Eq. (1) in the region $\tau > 0$. If it does hold true at $\tau > 10^{-2}$, it is only in a very narrow τ interval and with a larger value of the exponent α than in the case $\tau < 0$. This agrees with the con-

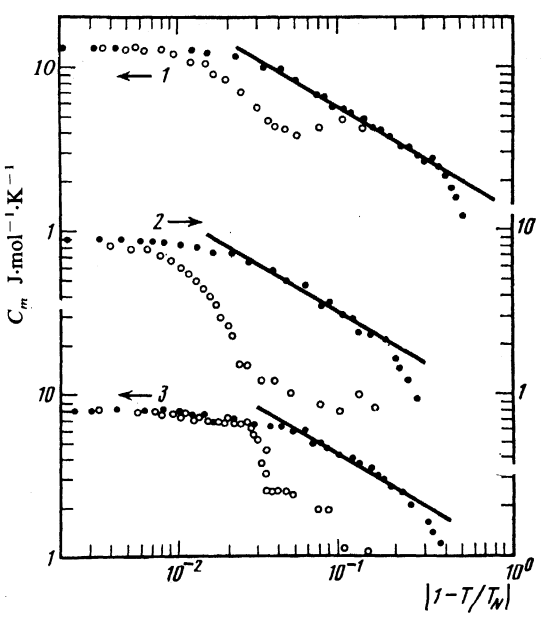

FIG. 4. Magnetic component of the heat capacity of the alloys $(Pd_xPt_{1-x})_3Fe$ vs $|1 - T/T_N|$. The dark and light circles are for $T < T_N$ and $T > T_N$, respectively. The values 1, 2, 3, correspond to $x = 0.16, 0.31$, and 0.47, respectively. The solid line is a plot of (1) at $\alpha = 0.58$.

clusions of Refs. 1 and 17. As T_N is approached, α decreases, as well as in the case $\tau<0$. In the interval $|\tau|<10^{-2}$ the $C_m(\tau)$ dependences are the same at temperatures above and below the Néel point.

Thus, the temperature dependences of the heat capacity and of the TCR indicate that they have a tricritical behavior in $(Pd_xPt_{1-x})_3Fe$ alloys at a palladium concentration in the vicinity of x_c. The magnetic state diagram of these alloys proposed in Ref. 7 can be refined by introducing, on the line of the phase transitions with respect to the AF parameter, a tricritical point at the concentration x_c. According to Refs. 1 and 17 we can understand also the observed concentration dependence of T_N. In the investigated alloys with concentrations $x=0$, 0.16, 0.31, and 0.47 the Néel temperatures are respectively 164, 163, 158.5, and 144.2. It must be indicated, however, that the formulas of the fluctuation theory[1,17] cannot describe exactly the temperature dependences of C_m and of the TCR near T_N.

In conclusion, we compare the measured heat capacities in the $(Pd_xPt_{1-x})_3Fe$ alloys with the earlier investigations of C_p in the analogous alloy system $Pt_3Mn_xFe_{1-x}$ (Ref. 14). It can be seen that the main features of the behavior of the heat capacity in the vicinity of the concentration phase transition F-AF are similar for both. One might conclude therefore that identical polycritical points are realized in these alloys at the critical concentration x_c. A more attentive examination of the results of the investigation of the set of physical properties shows, however, that in the $Pt_3Mn_xFe_{1-x}$ alloys the jump of the parameters $(T_c\text{-}T_N)$ in the vicinity of the concentration x_c is noticeably smaller[18] than in the $(Pd_xPt_{1-x})_3Fe$ system. It follows therefore that in the $Pt_3Mn_xFe_{1-x}$ alloys the polycritical point can be tetra- or bicritical. For alloys with a mixed exchange situation, such a situation was discussed theoretically in Ref. 19.

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