High temperature NMR experiments lend themselves easily to treatment with participation of FPR (Sec. 2) and yield quite reasonable values for their characteristics. Much attention is currently paid to NMR in the low-temperature region. It would be of interest to extend the scope of this research by performing experiments in the vacancion regime, i.e., accompanied by production of nonequilibrium vacancy densities. The results of Sec. 3 provide for this regime a theoretical description that can be used also in the search for zero vacancies.

I am deeply grateful to A. F. Andreev for attentive guidance and valuable advice, and to V.I. Marchenko for a helpful discussion.

## APPENDIX

Taking into account the discussion, in Sec. 3, of the solutions of Eqs. (3.17), we write down in explicit form only those functions $F_i$, $\Psi_i$, and $\Phi_i$, which are needed for the calculation of the imaginary part of the susceptibility (3.19):

$$F_0(\theta)=\frac{1}{\sin\theta}\left[\frac{\pi}{2}-\left(\frac{\pi}{2}+\ln 2-\ln\sin\theta\right)\cos\theta-\theta-\ln\operatorname{tg}\frac{\theta}{2}\right], \quad (A.1)$$

$$\begin{aligned}F_1(\theta)=\frac{1}{\sin\theta}\Big\{&\pi+\left(1-\frac{\pi}{2}\right)\ln 2-\frac{1}{2}\ln^2 2-\frac{\pi^2}{6}\\&+\cos\theta\left[\theta+\frac{\pi}{2}(\ln 2-1)+\frac{\pi^2}{6}-\frac{1}{2}\ln^2 2\right]-2\sin\theta\\&-\cos^2\theta\left(\ln\sin\theta+\frac{\pi}{2}+\ln 2\right)+\frac{1}{2}(1+\cos\theta)\ln^2(1+\cos\theta)-\ln(1+\cos\theta)\\&+\cos\theta\ln\sin\theta\left[2\cos\theta+\frac{\pi}{2}-\ln(1+\cos\theta)\right]+\ln\operatorname{tg}\frac{\theta}{2}\Big[\ln\sin\theta\\&+\theta-1-\frac{\pi}{2}-\left(\frac{\pi}{2}+\ln 2\right)\cos\theta\Big]-\ln^2\sin\theta+\left(\frac{\pi}{2}+\ln 2\right)\ln\sin\theta\\&-\int\ln\operatorname{tg}\frac{\theta}{2}\,d\theta-\cos\theta\int\frac{\ln(1+\cos\theta)}{1-\cos\theta}\,d\cos\theta-\cos\theta\int\theta\operatorname{ctg}\theta\,d\theta\Big\},\end{aligned} \quad (A.2)$$

$$\begin{aligned}\Phi_0(\theta)=\frac{1}{\sin\theta}\Big\{&\frac{\pi}{2}\left[1+\frac{\pi^2}{4}-\frac{\pi}{3}+\left(\frac{\pi}{2}-1\right)\ln 2\right]\\&-\frac{1}{2}\ln^2 2+\Big[\left(\pi-1+\frac{1}{2}\ln 2\right)\ln 2+\frac{\pi^2}{3}+\frac{\pi}{2}\left(1-\frac{\pi}{2}\right)\ln 2\\&-\frac{\pi}{2}-\frac{\pi^3}{8}\Big]\cos\theta+\left[\ln\operatorname{tg}\frac{\theta}{2}-\frac{\pi}{2}\left(1-\frac{\pi}{2}-\ln 2\right)\right]\sin\theta\\&+\left(1-\ln 2-\frac{\pi}{2}+\ln\sin\theta\right)\theta\sin\theta+(1-\ln 2)\Big(\ln\operatorname{ctg}\frac{\theta}{2}\\&+\cos\theta\ln\sin\theta\Big)+\theta\left[\left(1-\frac{\pi}{2}\right)\left(\frac{\pi}{2}+\ln 2\right)-\ln\sin\theta-1\right]\\&-\frac{\pi}{2}(1+\cos\theta)\ln(1+\cos\theta)-\frac{1-\cos\theta}{2}\ln(1+\cos\theta)\ln(1-\cos\theta)\\&+(2-\sin\theta)\int\theta\operatorname{ctg}\theta\,d\theta-\cos\theta\int\frac{\theta\,d\theta}{\sin\theta}+\int\frac{\ln(1-\cos\theta)}{1+\cos\theta}\,d\cos\theta.\end{aligned} \quad (A.3)$$

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Translated. by J. G. Adashko

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# Heat capacity of $Pt_3Mn_xFe_{1-x}$ alloys

N. I. Kourov, S. M. Podgornykh, Yu. N. Tsiovkin, and N. V. Volkenshteĭn

*Institute of Metal Physics, Ural Scientific Center, USSR Academy of Sciences*

(Submitted 7 May 1980)
Zh. Eksp. Teor. Fiz. 79, 1921–1926 (November 1980)

The adiabatic-calorimeter method is used to investigate experimentally the heat capacity of the atomically ordered alloys $Pt_3Mn_xFe_{1-x}$ ($x=0, 0.2, 0.3, 0.4, 0.5, 0.8, 1$) in the temperature interval 13–300 K. The alloys are antiferromagnetic at $x=0$ and ferromagnetic at $x=1$. The temperature and concentration dependences of the magnetic part of the heat capacity are discussed within the framework of the model of the nucleation mechanism of a concentration phase transition.

PACS numbers: 65.40.Em

It was shown by a number of workers[1,2] that a ferromagnetic-antiferromagnetic phase transition is produced in quasibinary solid solutions based on the atomically ordered $Pt_3Mn$–$Pt_3Fe$ alloys when the concentration of the magnetic components is varied at low temperatures. The initial alloys have at room temperature an fcc lattice with close parameters: $a=3.89$ Å, for the $Pt_3Mn$ alloy and $a=3.87$ Å for the $Pt_3Fe$ alloy. In the antiferromagnetic state at $T\leq T_N=164$ K the lattice of the $Pt_3Fe$ alloy becomes weakly tetragonal ($c/a=0.9998$). The $Pt_3Mn$ alloy is a collinear ferromagnet at $T\leq T_c$ ($T_c=390$ K).

The solid solutions $Pt_3Mn_xFe_{1-x}$ have at manganese concentrations $0.2 \leq x \leq 0.5$ a magnetic state characterized by the presence of two types of reflections on the neutron diffraction patterns; corresponding to a ferromagnetic (100) and antiferromagnetic ($\frac{1}{2}\frac{1}{2}0$) structure, respectively.[1] A similar picture is known to be observed also in the atomically ordered $Pt_3Fe$–$Pd_3Fe$ alloys.[3] The physical properties of these alloys in the region of the mixed state have a number of distinguishing features.[1-4] The present paper is devoted to an investigation of the heat capacity of alloys in which a phase transition from the anitferromagnetic into the ferromagnetic state takes place when the concentration of the components is changed.

The heat capacity of the alloys $Pt_3Mn_xFe_{1-x}$ ($x = 0, 0,2, 0.3, 0.4, 0.5, 0.8, 1$) was measured by the adiabatic-calorimeter method in the temperature interval 13–300 K with an error not larger than 1.5%. The samples, certified by neutron diffraction, were kindly supplied to us by V.V. Kelarev. The method used to produce and finish them are described in the relevant papers.[2]

## 1. EXPERIMENTAL RESULTS

The results of the measurement of the heat capacity $C_p$ at constant pressure as a function of the temperature are shown in Fig. 1. It is seen that $C_P(T)$ of the $Pt_3Fe$ alloy has a $\lambda$ anomaly near $T_N = 164$ K. The size of the heat-capacity peak, however, is insignificant. On going to alloys with $x = 0.2$ and 0.3, the heat capacitance at the maximum increases strongly. The $C_P(T)$ curve of the alloy with $x = 0.4$ shows two characteristic regions bounded by inflection points. It can be assumed that the observed anomalies of the heat capacity are governed by the magnetic states of the alloys.

In the general case the heat capacity can be expressed in the form

$$C_p = C_{lat} + C_m + C_{el} + C_{nuc} + C_{dil} \tag{1}$$

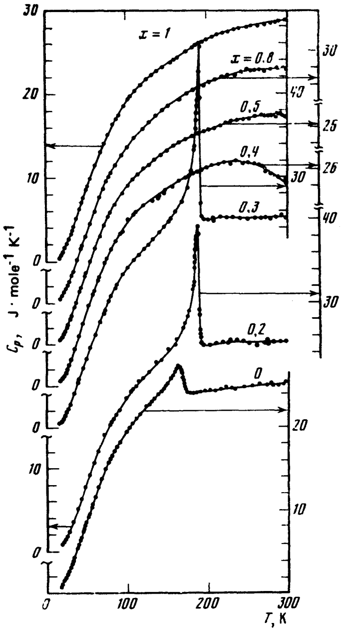

FIG. 1. Heat capacity of $Pt_3Mn_xFe_{1-x}$ alloys as a function of temperature.

where $C_{lat}$, $C_m$, $C_{el}$ and $C_{nuc}$ are respectively the lattice, magnetic, electronic, and nuclear contribution to the total heat capacity at constant volume ($C_v$). $C_{dil} = C_P - C_v$ is the dilation correction.

According to calculations made for the investigated alloys in the region of the magnetic phase transitions (100–300 K) the main contribution to the heat capacity is made by two terms, lattice and magnetic. The lattice contribution can be estimated in the Debye approximation if the Debye temperature $\Theta_D$ is known. For the $Pt_3Fe$ alloy, $\Theta_D = 258$ K and is determined by linear interpolation of the Debye temperatures of the initial components, describes satisfactorily the results of the measurements of the thermal-expansion coefficient.[5] Since the melting temperatures of the $Pt_3Mn_xFe_{1-x}$ alloys are approximately equal, it can be assumed, according to Ziman,[6] that $\Theta_D = 258$ K also for alloys with arbitrary manganese concentration. Thus, the lattice contribution to the heat capacity in the considered temperature region is assumed to be the same for all the investigated alloys.

The magnetic contribution to the heat capacity, obtained as the difference $C_P - C_{lat} = C_m$, is shown in Fig. 2. It is seen that besides the described anomalies on the $C_P(T)$ curves, which become more pronounced on the $C_m(T)$ curves, an appreciable magnetic contribution is observed in the heat capacity of the alloys with $x = 0.5$, 0.8, and 1 at temperatures above 100 K. Notice should also be taken of the shift of the heat-capacitance anomaly temperatures from 164 K for the alloy with $x = 0$ to 189 K at $x = 0.2$ and 191 K at $x = 0.3$. From a comparison of these data with those obtained by neutron diffraction[2] it is seen that the temperatures corresponding to the anomalies of $C_m(T)$ at $x = 0$, 0.2, and 0.3 are Néel points of the antiferromagnetic subsystem. In the heat capacities of the alloys with $x = 0.4$ and 0.5 however, there are no $\lambda$ anomalies at the temperatures close to 100 and 300 K corresponding to the vanishing of the antiferromagnetic reflection and the ferromagnetic reflection on the neutron-diffraction patterms. As follows from Fig. 2, smeared maxima are observed on the plots of $C_m$ against temperature are observed for these alloys in place of the characteristic peaks.

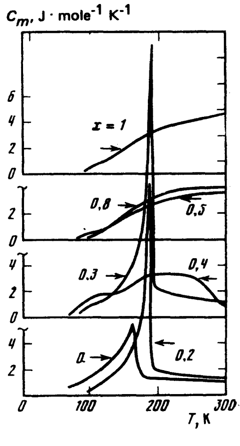

FIG. 2. Magnetic heat capacity of $Pt_3Mn_xFe_{1-x}$ alloys as a function of temperature.

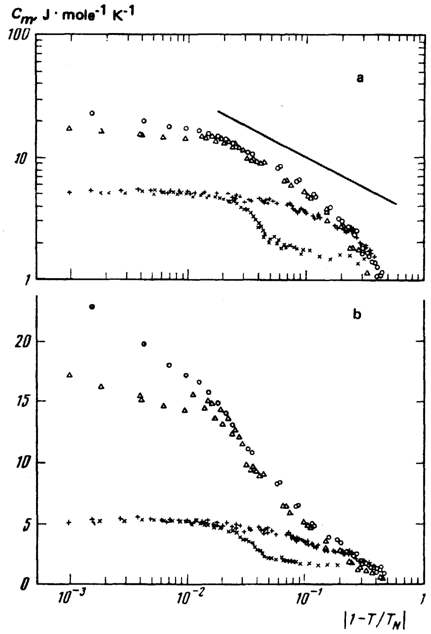

FIG. 3. Magnetic heat capacity of $Pt_3Mn_xFe_{1-x}$ alloys as a function of $|1 - T/T_N|$ in logarithmic (a) and semilogarithmic (b) coordinates. For $T<T_N$: +) $x=0$, Δ) $x=0.2$; 0) $x=0.3$. For $T>T_N$: ×) $x=0$. The solid line is a plot of (2) with $\alpha=0.5$.

To analyze the $C_m(T)$ curves of the alloys with $x=0$, 0.2, and 0.3, Fig. 3*a* shows in a logarithmic scale plots of their magnetic heat capacity against $\tau=(T-T_N)/T_N$. Since near-zero coefficient of log $\tau$ can correspond either to a tendency of $C_m$ to a constant limit or to a logarithmic increase, we show in Fig. 3b also plots of $C_m$ against log$\tau$.

Figure 4 shows the concentration dependence of $C_m$ at $T=240$ K, demonstrating the change of the heat capacities of the investigated alloys in the case of a paramagnet ferromagnet concentration phase transition. It is seen that near $x=0.4$ the magnetic heat capacity has a discontinuity, with $C_m$ of the ferromagnet larger than that of a paramagnet.

## 2. DISCUSSION OF RESULTS

The behavior of the heat capacity of the alloy $Pt_3Fe$ in the vicinity of $T_N$ is similar to that of the coefficient of thermal expansion, measured by Sumijama and Graham.[5] The observed anomaly at $T_N$ rounds off in an interval of two degrees from the phase-transition point. It is known that the fluctuation theory[7] predicts a power-law dependence of the magnetic heat capacity.

$$C_m \sim |\tau|^{-\alpha} \tag{2}$$

with an exponent $\alpha$ close to zero. According to Fisher and Langer,[8] such a temperature coefficient of electric resistivity (TCR) has the same power-law divergence. It was shown earlier[9] that the TCR of the atomically ordered $Pt_3Fe$ near $T_N$ has no fluctuation singularities and changes jumpwise.

It is seen from Fig. 3 that the heat capacity of the $Pt_3Fe$ alloy at $|\tau|<10^{-2}$ is constant. The assumption of a constant value by $C_m(T)$ in the immediate vicinity of the Nêel point is apparently determined by the presence, in the antiferromagnet, of inhomogeneities that serve as boundaries of the correlation region. Such inhomogeneities can be iron atoms in excess of stoichiometry, as well as ordering domain walls.[9] The presence of excess iron (~1 at. %) was revealed by chemical analysis and also by the difference between the Nêel temperature of our sample (164 K) and that of the practically stoichiometric alloy $Pt_3Fe$ (170 K).[10] For the indicated finite correlation regions there can take place both a volume dependence of the ordering temperature (the so-called relative shift), and a relative "smoothing." The indicated types of distortions with respect to a phase transition in an infinite system lead, in our opinion, to a smoothing of the heat-capacity anomalies and to the absence of fluctuation singularities of the TCR near $T_N$.

Comparing the temperature dependences of the magnetic heat capacity of the $Pt_3Mn_xFe_{1-x}$ alloys with the TRC of analogous alloys $(Pd_xPt_{1-x})_3Fe$ in the transition region of the concentrations, it is easy to verify that their behavior in the vicinity of the Nêel point is similar. For both $C_m$ and the TCR one observes, with increasing concentration $x$ in the alloy, first a considerable increase in the anomaly near $T_N$, followed by a smearing of the anomaly at the assumed $T_N$.

When the concentration of the components changes, ferromagnetic clusters (nuclei of a new phase[4]) are produced with a probability $P(x)$ in the antiferromagnetic matrix. The value of $P(x)$ is determined by the Bernoulli distribution, which sets the probability of having, among the $Z$ nearest neighbors of a given atom, $n_0$ or more atoms of a definite sort when the concentration of these atoms is $x$. In the alloys $Pt_3Mn_xFe_{1-x}$ the ferromagnetic clusters are produced when $n \geqslant n_0$ manganese atoms are present in the nearest surrounding of the iron atom. At a certain concentration $x_{cr}$ averaged over the crystal, the probability of formation of ferromagnetic regions is equal to the probability of the appearance of antiferromagnetic regions. In this case the alloys have an antiferromagnet as the solvent matrix at $x<x_{cr}$ and a ferromagnet at $x>x_{cr}$.

The appearance of ferromagnetic nucleation centers in an antiferromagnetic matrix is accompanied by the appearance of a surface energy of the nuclei as well as by a change of the elastic energy in the crystal. An estimate of the internal pressure near $x_{cr}$, obtained earlier[12] for $(Pd_xPt_{1-x})_3Fe$ alloys, shows that it reaches tens of kilobars. In this case the concentration, just as the pressure, can alter the state of the antiferromagnetic subsystem. It can happen that a second-order phase transition takes place at certain pressures, and one of first order at others. The transition between these phenomena occurs in a tricritical point. The heat capacity of alloys near such a point is described at $\tau<0$ by relation (2) with exponent $\alpha=0.5$.[13] Larkin and Pikin[14] have shown that allowance for the compressibility and for the interaction with the acoustic phonons leads to a first-order phase transition close to one of second order. At low striction near the transition tem-

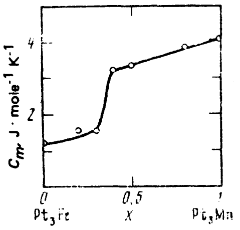

FIG. 4. Magnetic heat capacity of alloys vs. the manganese concentration at $T = 240$ K.

perature ($\tau > 0$) the heat capacity of such a system diverges logarithmically, and far from it it has the power-law dependence (2) with $\alpha = 0.5$.

As seen from Fig. 3, at $\tau < 0$, in the immediate vicinity of $T_N$ ($|\tau| < 2 \times 10^{-2}$), the magnetic contribution to the heat capacity is described by the relation (2) with exponents $\alpha = 0.06$ for the alloy with $x = 0.2$ and $\alpha = 0.156$ for the alloy with $x = 0.3$. With increasing $|\tau|$ the value of the exponent for these changes, and becomes close to 0.5 in the interval $2 \times 10^{-2} < |\tau| < 2 \times 10^{-1}$. This is seen in Fig. 3a, where the solid line shows for comparison a plot of (2) with $\alpha = 0.5$.

At $\tau > 0$, in alloys with $x = 0.2$ and 0.3, the magnetic heat capacity decreases practically jumpwise to a certain limit, and depends little on temperature with further increase of $|\tau|$. The behavior of $C_m$ of these alloys at $\tau > 0$ is governed apparently by the fact that the phase transition at the Nêel point is a transition into an inhomogeneous magnetic state characterized by the presence of ferromagnetic clusters in a paramagnetic matrix. This determines the asymmetry of the temperature dependence of $C_m$ of the considered alloys relative to $T_N$.

Particular interest attaches to the alloys with $x = 0.4$ and 0.5. An investigation of the magnetic and neutron-diffraction properties[1,2] shows that the state of their antiferro- and ferromagnetic subsystems is essentially inhomogeneous. However, the Nêel and Curie points of these alloys could be determined from the vanishing of the neutron diffraction reflections.[1,2] On the plots of the magnetic heat capacity against temperature, these phase-transition points correspond to strongly smeared maxima.

It follows from Fig. 4, where the concentration dependence of $C_m$ is plotted at a temperature from the range $T_N < T < T_c$, a phase transition from the paramagnetic into the ferromagnetic state is realized near $x = 0.4$. It can be assumed that this concentration is close to $x_{cr}$ and is the point of intersection of the order parameters of the subsystem. As shown by Izyumov, Skryabin, and Laptev,[15] at such a point the phase transition becomes indeterminate when the temperature is varied, and the characteristic features become smeared out. Therefore a smearing of the anomalies of $T_N$ and $T_c$ is observed for the alloys with $x = 0.4$ and 0.5, which lie in the vicinity of the point of intersection of the order parameters.

We note in conclusion that the heat capacity investigated in this paper reflects the distinguishing features of the magnetic states of alloys with exchange interactions of opposite sign. The behavior of $C_m$ near the Nêel point in alloys with $x < x_{cr}$ is determined by the interaction between the antiferro- and ferromagnetic subsystems.

In alloys with concentration near $x_{cr}$, owing to the inhomogeneity of their magnetic state, the phase-transition points of the magnetic subsystems are not very pronounced on the Cm($T$) curves.

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Translated by J. G. Adashko