

Thermoelectric power of PdMn alloys: the phonon-drag effect

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(Submitted 6 October 1982)

Zh. Eksp. Teor. Fiz. **85**, 561–567 (August 1983)

A study was carried out of the thermoelectric power of PdMn alloys with Mn concentrations in the range 0.81–10 at. % in the temperature range 15–100 K. It was shown that both diffusion thermoelectric power and phonon-drag thermoelectric power undergo a substantial change in the course of the ferromagnetism→spin glass transition ($c \approx 4\text{--}5$ at. % Mn) which occurs in these alloys. The connection established between the phonon-drag thermoelectric power and the nature of the d -band suggests that this transition is accompanied by a rearrangement of electron structure, i.e., the disappearance of hole, open, and intersecting cylinders that are characteristic of the Fermi surface of palladium. This distinguishes the above ferromagnetism→spin glass transition from the analogous transition for $c < 0.1$ at. % Mn in which a genetic relationship is preserved between the band structures of the PdMn alloys and palladium.

PACS numbers: 72.15.Jf, 71.25.Mg, 75.30.Kz

PdMn alloys undergo a ferromagnetism→spin glass transition in the region of 4–5 at. % Mn, which is due to the presence of two types of Mn-Mn interaction, namely, long-range ferromagnetic and short-range antiferromagnetic.¹ Studies of the resistivity of these alloys² and calculations of the band structure of the analogous NiMn systems³ have shown that the transition is accompanied by the rearrangement of the d -band. It is therefore expected that other properties that are directly related to the band structure will exhibit considerable changes during the ferromagnetism→spin glass transition. These properties include thermoelectric power. The role of the d -band is reflected in the thermoelectric power in two ways. First, since it determines the density of states, the d -band determines the diffusion thermoelectric power (S_d) and, second, the d -electrons participate in the relaxation of the phonon system and are thus responsible for the phonon-drag thermoelectric power (S_{pd}).

The aim of this paper is to establish the role of the d -band in the formation of the phonon-drag thermoelectric power and in the changes that occur in the latter during the transition from palladium to the ferromagnetic and the spin-glass state of the PdMn alloy system.

We have measured the thermoelectric power of PdMn alloys with concentrations in the range 0.81–10 at. % Mn for temperatures in the range 15–100 K. This choice of temperature and concentration was dictated by the following considerations. First, these alloys exhibit the ferromagnetism→spin glass transition. Second, the phonon-drag thermoelectric power is at a maximum in this temperature range. Third, the temperature range that we have chosen lies above the magnetic ordering temperature (the ordering temperature of these alloys is less than 13 K, Ref. 2), so that there are no contributions to the thermoelectric power that are characteristic of magnetically ordered phases. Fourth, there are no structural transformations in these alloys that produce radical differences in the crystal structures of PdMn alloys and palladium.

RESULTS OF MEASUREMENTS AND DISCUSSION

The thermoelectric power was measured by the differential method described in Ref. 4. Figure 1 shows the thermoelectric power of PdMn alloys as a function of temperature. It is clear that, for concentrations below 6 at. % Mn, the thermoelectric power has a maximum between 50 and 70 K that is analogous to the corresponding maximum for palladium and most of its dilute alloys.^{5–7} The maximum is absent for concentrations in excess of 6 at. % Mn and, for them, we have the characteristic linear variation of thermoelectric power with temperature.

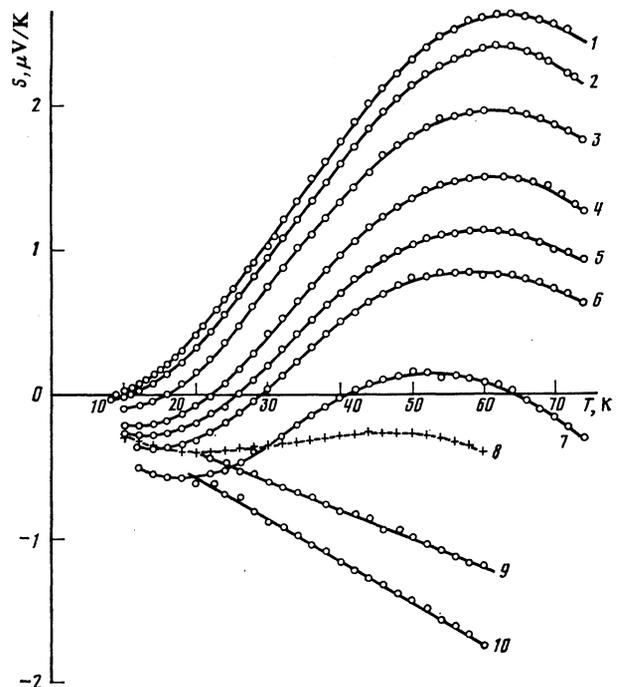


FIG. 1. Temperature dependence of the thermoelectric power of PdMn alloys: 1—0.81, 2—1.25, 3—1.65, 4—2.1, 5—2.6, 6—3, 7—3.75, 8—5, 9—7, 10—8 at. % Mn.

The measured thermoelectric power is the sum of the phonon-drag and diffusion thermoelectric powers. The diffusion thermoelectric power is a linear function of T in this temperature range. This follows from the following. First, the dominant scattering mechanism is elastic scattering by impurities, since ρ_T ($T < 40$ K) = $(10^{-1}-10^{-2})\rho_0$, where ρ_T and ρ_0 are the thermal and residual resistivities of the alloys. Second, the effect of temperature spreading of the Fermi distribution function and of the shift of the chemical potential on the thermoelectric power, which results in its nonlinear temperature dependence, is quite small in this temperature range. We have therefore plotted $S(T)/T$ as a function of temperature in order to separate the phonon-drag and diffusion components of the thermoelectric power (Fig. 2). Extrapolation of the $S(T)/T$ curves to $T = 0$ (shown by the dashed lines in the figure) gives $\alpha = S_d/T$, and the phonon-drag contribution is given by $S(T)/T - \alpha$.

It is clear from Fig. 2 that the thermoelectric power $S(T)$ is described by a linearly quadratic function in the temperature interval 15–30 K. The quadratic temperature dependence of S_{pd} reflects the transition from the cubic relation $S_{pd} \sim T^3$, which is characteristic for $T \ll T_D$ (T_D is the Debye temperature), to the maximum of S_{pd} , which occurs to $T = 0.1T_D - 0.2T_D$.⁸ The concentration dependence of the phonon-drag thermoelectric power may be characterized either by $\beta = S_{pd}(T)/T^2$ or by the size of the S_{pd} maximum.

It is clear from Fig. 2 that, for Mn concentrations between 0.81 and 3.75 at.%, the $S(T)/T$ curves have the same

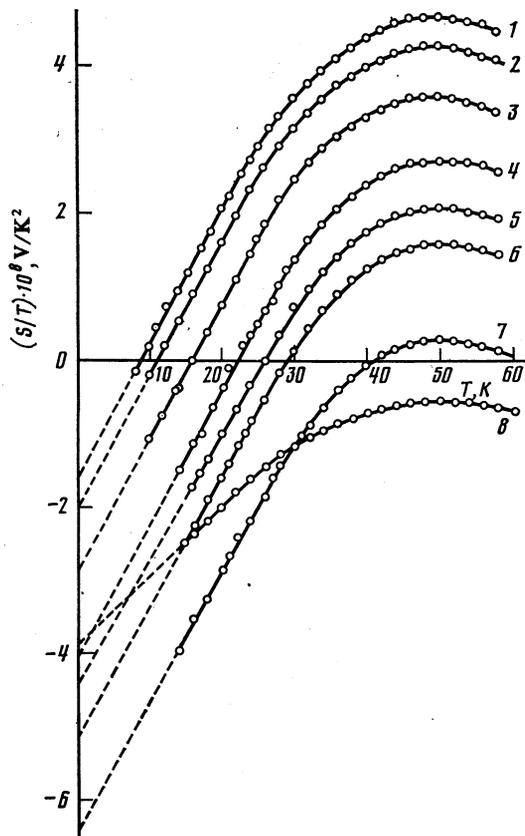


FIG. 2. Temperature dependence of the ratio $S(T)/T$ of PdMn alloys: 1—0.81, 2—1.25, 3—1.65, 4—2.1, 5—2.6, 6—3, 7—3.75, 8—5 at.% Mn.

shape in the range 15–80 K, and can be superimposed by a shift parallel to the ordinate axis. In other words, the phonon-drag thermoelectric power of these alloys remains constant up to 3.75 at.% Mn, and all the changes in the thermoelectric power are connected exclusively with changes in the diffusion thermoelectric power. For $c > 3.75$ at.% Mn, the maximum on the $S(T)/T$ curves is sharply reduced, and $S(T)$ becomes a linear function of T for concentrations in excess of 6 at.% Mn (Fig. 1). If we compare this behavior of S_{pd} with the magnetic diagram, we may conclude that the phonon-drag thermoelectric power does exist in the ferromagnetic PdMn alloys and is independent of concentration. In the ferromagnet→spin glass transition region, S_{pd} is found to fall sharply and vanishes altogether in the spin glass state.

To elucidate the reasons for this type of behavior of the phonon-drag thermoelectric power of PdMn alloys, let us consider the nature of the phonon-drag thermoelectric power of palladium. It was suggested in Ref. 9 that the positive values of S_{pd} of palladium and its alloys are due to phonon-induced s - d or d - d hole transitions. Analysis of the thermoelectric power of PdPt alloys⁷ suggests that the latter mechanism is to be preferred, i.e., one can assume a strong phonon- d -electron interaction which determines these transitions. Neutron-scattering studies of the phonon spectrum of palladium may serve as direct confirmation of this. It is shown in Refs. 10 and 11 that the anomalies in phonon dispersion and the peak on phonon-line broadening curves, which are observed for palladium, are due to the presence of strong phonon- d -electron interaction in which d - d transitions take place on hole sheets of the Fermi surface forming a grid of open and mutually intersecting cylinders.¹¹ This enables us to conclude that the nonequilibrium phonon system in palladium relaxes as a result of such d - d transitions, and this is responsible for the observed phonon-drag thermoelectric power.

In dilute alloys, the phonon-drag thermoelectric power may be different from the S_{pd} of the host because the parameters of the phonon and electron systems of such alloys may be different from the analogous parameters of the host. Moreover, an additional source of relaxation of the phonon system is present in the alloys, namely, phonon-impurity scattering which, under certain definite conditions, leads to a reduction in the probability of phonon-electron scattering and, consequently, to a reduction in the effects of phonon drag.

For the PdMn alloys that we have investigated, we have found that the phonon-drag thermoelectric power does not vary with increasing concentration of manganese up to 3.75 at.% (Fig. 3). The recorded singularity on the $S_{pd}(c)$ curve is not exclusively characteristic of ferromagnetic PdMn alloys. It occurs for other palladium alloys for which it has been found that S_{pd} is independent of concentration up to 10 at.% Pt in PdPt alloys,⁷ and up to 20 at.% Au in PdAu alloys.⁵ Moreover, it is found that, in the temperature range 10–20 K, the values of S_{pd} for these alloys are practically equal to the value of S_{pd} for palladium, just as in the case of the PdMn alloys that we have investigated. In addition, the estimated

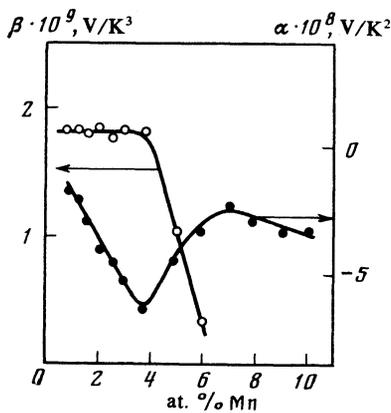


FIG. 3. Concentration dependence of the diffusion thermoelectric power ($\alpha = S_d/T$) and the phonon-drag thermoelectric power ($\beta = S_{pd}/T^2$) of PdMn alloys.

maximum phonon-drag thermoelectric power of palladium, obtained by using the diffusion thermoelectric power at high temperatures, has shown that its value and the maximum value S_{pd} for PdMn alloys ($c < 3.75$ at. % Mn) are practically equal.²⁾ This enables us to consider that the nature of the phonon-drag effects in palladium alloys and, in particular, in the ferromagnetic PdMn alloys, is the same as in palladium. It is connected with the presence of both the strong phonon- d -electron interaction and of the open hole cylinders that are characteristic of the Fermi surface of palladium. Neutron diffraction studies of ferromagnetic PdFe alloys¹³ provide a direct confirmation of this. The phonon spectrum anomalies found for these alloys, which are analogous to the phonon-spectrum anomalies in the case of palladium, indicate that the introduction of Fe atoms into palladium at concentrations less than 10 at. % Fe does not result in any radical changes in the band structure or the phonon- d -electron interaction, so that the mechanism responsible for the relaxation of the phonon system is the same as in the case of palladium.

As noted above, the interesting feature of the phonon-drag thermoelectric power of the PdPt and PdAu alloys and the ferromagnetic PdMn alloys is the absence of any appreciable effect of phonon-impurity scattering in a broad range of concentrations. This behavior is connected with the fact that, in the temperature range in which these measurements were performed, the phonon system relaxes mainly via the electrons, and the probability of scattering of long-wave phonons by impurities, which determines the phonon-drag effect, is small.¹⁵ We therefore consider that, in the PdMn alloys that we have examined, phonon-impurity scattering processes have little effect on the phonon-drag thermoelectric power and do not govern its behavior in the magnetic transition region in which a sharp change in S_{pd} has been observed. Bearing this in mind, and assuming that the changes in the d -band of PdMn alloys with $c < 3.75$ at. % Mn are slight (in addition to the neutron interaction studies, this also confirms measurements of the resistivity of these alloys²⁾), it becomes clear why the phonon-drag thermoelectric power is present in the ferromagnetic PdMn alloys and is independent of concentration.

Using the above analysis of the phonon-drag thermoelectric power of PdMn alloys with concentrations below 3.75 at. % Mn, we can readily establish the reasons why it vanishes in the course of the transition to the spin glass state. The observed reduction in the phonon drag thermoelectric power in the region 4–6 at. % Mn, and its absence in the PdMn spin glass, reflect the rearrangement of the band structure that accompanies the ferromagnet→spin glass transition. The hole cylinders that are characteristic for the Fermi surface of palladium and the thermomagnetic PdMn alloys disappear as a result of this rearrangement and, consequently, the mechanism responsible for the relaxation of the phonon system that is characteristic for palladium disappears as well.

The change in the band structure that accompanies this magnetic transition is also indicated by measurements of resistivity² and diffusion thermoelectric power. Figure 3 shows the diffusion thermoelectric power of the PdMn alloys as a function of concentration. It is clear that, as the Mn concentration increases up to 3.75 at. %, the thermoelectric power S_d falls almost linearly. It rapidly increases in the range 4–6 at. % Mn and thereafter falls again in the spin-glass state. Comparison of the concentration dependence of the diffusion thermoelectric power of the PdMn alloys that we have obtained with the analogous function $S_d(c)$ for the ferromagnetic PdFe(PdCo) alloys¹⁶ suggests that the non-monotonic variation in the diffusion thermoelectric power in the range 4–6 at. % Mn, in which the ferromagnetism→spin glass transition takes place, is due to the rearrangement of the band structure, namely, a change in the density of states. This is also indicated by the different behavior of the concentration dependence of the diffusion thermoelectric power, namely, different rates of variation with increasing concentration, which reflects differences in the band structures of these states. It is important to emphasize that there is a direct connection between the behavior of the diffusion thermoelectric power and the phonon-drag thermoelectric power. Since the hole cylinders on the Fermi surface provide the main contribution to the density of states, and it is precisely with these cylinders that the phonon-drag effects are connected, the disappearance of these cylinders in the course of the photomagnetism→spin glass transition leads to a sharp change in the diffusion thermoelectric power.

In principle, the changes in band structure, observed for the PdMn alloys during the ferromagnetism→spin glass transition, can be understood if we suppose, by analogy with the similar NiMn system,³ that, depending on the nature of their immediate environment, the magnetic states of the Mn atoms are different, so that these atoms provide a number of different partial contributions to the density of states. The ferromagnetism→spin glass transition is accompanied both by a change in these contributions and in their ratios, so that they should have a definite influence on the partial contribution of the palladium atoms to the density of states. It may therefore be considered as established that this magnetic transition results in a loss of the genetic connection between the band structure of the PdMn alloys and the band structure of palladium, and the rearrangement of the electron

structure during the transition from palladium to the anti-ferromagnetic PdMn alloys (for $c > 15$ at. % Mn, the PdMn alloys are antiferromagnets) begins to occur in the region of the ferromagnetism→spin glass transition.

Let us now exploit the phonon-drag thermoelectric power to investigate band structure, and consider the ferromagnetism→spin glass transition that occurs in the PdMn alloys at low Mn concentrations ($c < 0.1$ at. %). The fact that S_{pd} of ferromagnetic PdMn alloys is independent of concentration and is equal to its value for palladium, which we have demonstrated, indicates that the low-concentration spin glass→ferromagnetism transition in these alloys is not accompanied by a rearrangement of the band structure. (The band structure of PdFe alloys behaves in a similar way during the spin glass→ferromagnetism transition for $c < 0.1$ at. % Fe, as indicated by measurements of the thermoelectric power of these alloys¹⁶ and by neutron scattering data.¹³) This behavior of the band structure of dilute PdMn alloys is due to the fact that the Mn atoms in the alloys have not as yet formed their own band, so that their contribution to the overall band-structure picture and their effect on the partial contribution to the band structure of the palladium atoms are small. It is therefore natural to expect that changes in the band structure that are connected with the Mn atoms during the low-concentration spin glass→ferromagnetism transition will have little effect, especially on properties due to the palladium band. In the range 4–6 at. % Mn, the contribution to the band structure due to the Mn atoms becomes considerable, and one can then speak of the band connected with manganese. Moreover, calculations³ have shown that this band undergoes a substantial change during the ferromagnetism→spin glass transition, and is partly responsible for the change in the contribution to the band structure due to the palladium atoms.

CONCLUSIONS

The foregoing analysis of the thermoelectric power of magnetically ordered PdMn alloys has enabled us to establish a connection between phonon drag effects and the electronic structure of these alloys. Thus, the origin of the phonon-drag thermoelectric power of ferromagnetic PdMn alloys is the same as in the case of palladium, and is connected with the relaxation of the phonon system through the d -hole sheets of the Fermi surface, which form a grid of open and mutually intersecting cylinders. These sheets of the Fermi surface disappear during the ferromagnetism→spin glass transition ($c \approx 4$ –6 at. % Mn), and this leads to a reduction in the phonon-drag thermoelectric power to zero.

The example of these alloys shows that, because of the presence of the strong phonon- d -electron interaction, the

phonon-drag thermoelectric power reflects the specific features of the electronic structure, and may therefore serve as a basis for a method of studying the band structure of transition metals and alloys.

¹This is in agreement with the results reported in Ref. 12, where it is shown that, in transition metals and alloys in which the d -band plays a determining role in the density of electron states, and the Fermi surface is highly isotropic, the d -electrons provide the main contribution to the electron-phonon interaction, and determine the shape of the phonon spectrum of these systems.

²These features in the behavior of the thermoelectric power of palladium and its alloys show that the "spurious" phonon drag model¹⁴ cannot be used to describe the function $S(T)$ for these systems. Actually, the "spurious" phonon drag thermoelectric power, which is determined by coherent electron-phonon (in metals) or electron-phonon-impurity (in alloys) scattering processes should be substantially different both for palladium and its alloys, and for different palladium alloys. Moreover, in the case of alloys, it should vary with concentration as $\rho_0/\rho_0 + \rho_T$, and should not be equal to the thermoelectric power of the host. The above experimental data indicate that this is not the case. It may, therefore, be concluded that, for palladium and the PdMn alloys, the nonlinear dependence of the thermoelectric power at low temperatures and its maximum in the range 50–70 K are due to real phonon-drag effects.

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Translated by S. Chomet