# Magnetocaloric effect in a superparamagnet

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Measurements have been made of the magnetocaloric effect in a superparamagnet. The object of investigation was a highly disperse powder of a ferromagnetic alloy based on the system Fe—Ni—Al. Upon adiabatic switching on of a magnetic field of intensity 10 kOe, the temperature of the specimen rose in the Curie point region by $\Delta T \sim 0.03°$. The results obtained justify the conclusion that the highly dispersed fraction consists essentially of particles of a single one of the phases of the alloy (the weakly magnetic phase $\beta_2$), which exhibit superparamagnetic properties also in the original (monocrystalline) specimen.

1. The study of the magnetic properties of superparamagnets is important both in relation to theory and from a practical point of view. The theory of the magnetism of this class of magnets is still very poorly developed. Meanwhile, in the interpretation of the magnetic properties of a whole series of practically important ferromagnets it is necessary to take account of the presence in them of superparamagnetic regions. In such a situation it is necessary to carry out investigations in which the potentialities of various experimental methods are exploited.

Valuable information about the properties of magnetically ordered systems can be obtained by measurement of the magnetocaloric effect. This effect has not been applied hitherto for investigation of the properties of superparamagnetic regions in magnetic alloys (or of actual superparamagnets).

2. We have conducted investigations of the magnetic properties of an alloy on the basis of the system Fe—Ni—Al. A characteristic property of this alloy is that it consists of two magnetic phases whose properties differ sharply. One of these, $\beta$, is ferromagnetic; its Curie point $T_{c\beta}$ occurs at about 1100°K. The other phase $\beta_2$, as was shown earlier,[1,2] has a Curie point $T_{c\beta_2}$ around 400°K, below which it reveals superparamagnetic properties; at higher temperatures, it becomes paramagnetic.

The basic object of investigation was a powder with a high degree of dispersion, obtained by mechanical grinding of the original ferromagnetic alloy. The highly dispersed fraction was separated by repeated centrifuging of a suspension of the powder in alcohol. Along with the measurements of the magnetocaloric effect in the highly dispersed fraction, similar investigations were also made on a monocrystal of the alloy. The basic purpose of this experiment was to explain the characteristic features of the temperature dependence of the magnetocaloric effect $\Delta T$ for subsequent comparison with the data for the highly dispersed powder. Here it was proposed to establish a correlation between the magnetic properties of the highly dispersed fraction and of the original ferromagnetic alloy; this was especially important in connection with the elucidation of the problem of the individual properties of phases $\beta$ and $\beta_2$. In addition, measurements were made of the magnetization curves $\sigma(T)$ and of the Mössbauer spectra of the $Fe^{57}$ nuclei.

3. According to the data from measurement of the magnetic moment of the highly dispersed specimen at 86°K in a pulsed magnetic field of intensity up to 120 kOe (Fig. 1a), the particles of the fraction are superparamagnetic. The dependence of the magnetic moment of the specimen on the field H is described quite satisfactorily by the Langevin function; the characteristic magnetic moment $m_0$ of the superparamagnetic particles is equal to approximately 100 $\mu_B$. The data on the Mössbauer effect also attest to the superparamagnetic properties of the particles of the highly dispersed fraction. At room temperature (that is, considerably below the Curie points of both phases of the alloy), the Mössbauer spectrum of the $Fe^{57}$ nuclei is a quadrupole doublet, whose components differ somewhat in intensity (Fig. 1b).

Figure 1c shows the temperature dependence of the change of temperature $\Delta T$, for the highly disperse specimen, on adiabatic switching on of a magnetic field of intensity H = 10 kOe. On the curve $\Delta T(T)$, a maximum is clearly evident in the vicinity of $T = T_{c\beta_2}$. In conjunction with the other data of Fig. 1, this can serve as a proof that the highly dispersed fraction is appreciably enriched in the phase $\beta_2$. In addition, the presence of this maximum, which has a form characteristic of ferromagnets, shows that the dimensions of the regions of phase $\beta_2$ in some particles of the fraction are large enough so that they display ferromagnetic properties. But their contribution to the total magnetic moment in sufficiently large fields is relatively small both in the original specimen[2] and in its highly dispersed fraction (Fig. 1a).

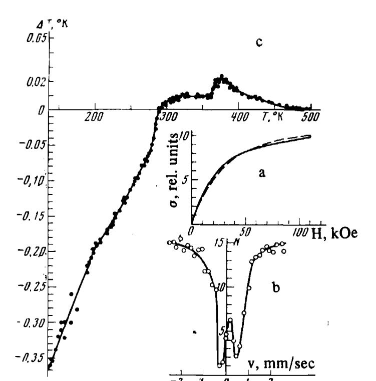


FIG. 1. a—magnetization curve of the highly dispersed fraction in a pulsed field at T = 86°K. The dotted curve is the Langevin function. b—Mössbauer spectrum of the same fraction at T = 300°K. Radiation source, $Co^{57}$ in Pd matrix. c—temperature dependence of the magnetocaloric effect in a superparamagnet (highly dispersed fraction of the alloy).

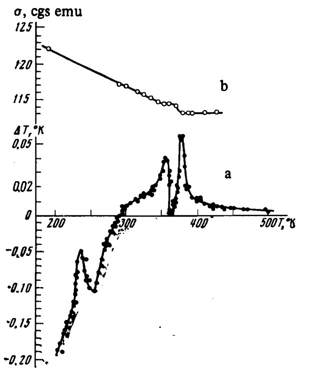


FIG. 2. a—temperature dependence of the magnetocaloric effect for a monocrystalline specimen of the alloy (composition, weight %: 33.1 Fe; 14.9 Ni; 7.8 Al; 35.5 Co; 5.2 Ti; 3.5 Cu). b—temperature dependence of specific magnetization of the monocrystal in external magnetic field H = 13 kOe.

The alloy investigated (which belongs to a group of alloys widely applied as material for permanent magnets) possesses uniaxial magnetic anisotropy. Therefore the value of the magnetocaloric effect is determined not only by the part of it due to the paraprocess, but also by a component caused by the energy of crystallographic magnetic anisotropy:[3]

$$\Delta T = \Delta T_{\text{para}} + \Delta T_{\text{an}}.$$

The change of sign of the effect on the $\Delta T(T)$ curve at $T \lesssim 290^\circ K$ indicates a strong temperature dependence of the magnetic anisotropy constant of the superparamagnetic particles in this temperature range.

Thus the $\Delta T(T)$ dependence for a superparamagnet in this case reflects both the strictly magnetic properties (in particular, the presence of a Curie point) and their connection with peculiarities of the crystalline structure (since in the magnetocaloric effect its anisotropy component $\Delta T_{an}$ is detected).

4. It is interesting now to compare the data for the superparamagnetic fraction with the results of the investigation of the original alloy. Figure 2a shows the $\Delta T(T)$ dependence for a monocrystalline specimen whose easy axis was oriented along the magnetic field. This orientation of the specimen was chosen in order to reduce to a minimum the anisotropy part of the effect $\Delta T_{an}$, against the background of which the part due to the paraprocess $\Delta T_{para}$ can be greatly obscured.

Although a reversal of sign of $\Delta T(T)$ is nevertheless observed, in the region of positive values of $\Delta T$ the temperature dependences of the magnetocaloric effect and of the magnetization (Figs. 2a and b) correlate quite well. It is easy to show this by using the known thermodynamic relation for the part of the magnetocaloric effect that is due to the paraprocess:

$$\Delta T_{\text{para}} = -\frac{T}{C_{pH}}\left(\frac{\partial\sigma}{\partial T}\right)_{pH}\Delta H$$

($\sigma$ is the specific magnetization of the specimen, $C_{pH}$ the specific heat). The maximum on the $\Delta T(T)$ curve for the monocrystalline specimen in the $T_{c\beta_2}$ region splits, in accordance with the profile of the $\sigma(T)$ curve; this indicates the unusual character of the magnetic transformation. The peculiarities of the magnetic transformation must apparently be related to interaction of phases $\beta$ and $\beta_2$ in the alloy, since on the $\Delta T(T)$ curve for the superparamagnetic fraction no splitting of the maximum in the $T_{c\beta_2}$ region is observed.

Despite the fact that in the original speciman, along with regions of phase $\beta_2$, there are also precipitations of phase $\beta$, the maximum on the $\Delta T(T)$ curve in the $T_{c\beta_2}$ region has about twice as large a value as for the highly dispersed fraction. This is due to the difference between the characteristic magnetic moments of the superparamagnetic particles in the specimens: in the case of the monocrystal $m_0 \approx 400\ \mu_B$,[2] whereas for the highly dispersed fraction, as was pointed out above, it amounts to only 100 $\mu_B$.

The large value of the negative magnetocaloric effect in the monocrystal is apparently due to the following causes. First, the geometry of the phase regions in the alloy is not completely regular, so that the directions of the precipitations have some scatter about the easy axis of the crystal. Second, there is known to be a contribution from a certain inaccuracy of orientation of the specimen in the magnetic field, and also from the not completely regular shape of the specimen. The non-monotonic behavior of the $\Delta T(T)$ curve in the region of negative values of the effect (Fig. 2a) is probably due to the presence in the monocrystal of the strongly magnetic phase $\beta$. It is significant that in the highly dispersed fraction, this peculiarity is absent (Fig. 1c).

5. Thus it can be stated that the magnetocaloric effect in a superparamagnet is completely measurable. In addition, another result of this investigation is also important: in our experiment, we succeeded in separating particles of phase $\beta_2$, which in the original specimen were already basically superparamagnetic. Finally, it has been shown by measurements of the magnetocaloric effect that superparamagnetic particles obtained by mechanical grinding of the alloy possess crystallographic magnetic anisotropy, as did the original specimen of the alloy.

In closing, we thank I. K. Kikoin for his interest in the research.

[1]V. M. Belova, V. I. Nikolaev, S. Yu. Stefanovich, and S. S. Yakimov, Fiz. Tverd. Tela 11, 3662 (1969) [Sov. Phys.-Solid State 11, 3078 (1970)].
[2]V. M. Belova, V. I. Nikolaev, and V. M. Stuchebnikov, Fiz. metallov i metallovedenie 34, 646 (1972).
[3]S. V. Vonsovskiĭ, Magnetizm (Magnetism), Nauka, 1971.

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188