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THE MAGNETOCALORIC BEHAVIOR IN NANOCRYSTALLINE MATERIALS

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Magnetocaloric behavior in nanocrystalline grains is studied as a consequence of magnon-phonon interactions. The field dependence for energy of quasiparticles is given. The sign of magnetocaloric effect in the vicinity of ferromagnetic phase transition and the possibility of the superferromagnetism in nanocrystalline materials is discussed.

1. Introduction

This paper will discuss some consequences of nanocrystalline magnetic structure on thermodynamical phenomena. We will use the simple approximation of magnon-phonon magnetoelastic interaction and discuss the transfer of energy between phonons and magnons in the vicinity of the phase transition given by enforcing the magnetic moment of nanocrystal into the direction perpendicular to the easy axis.

At the end we shall discuss the possibility of a superferromagnetism in nanocrystalline materials.

2. Models and calculations

As the nanocrystalline samples we consider the samples of amorphous magnetic material containing small crystals from the same material. The crystals are supposed to have magnetic uniaxial anisotropy. The crystal grains have size of 10-40 nm. Such nanocrystals contain approximately $10^4 - 10^6$ atoms with nonzero magnetic moments (example of such material could be the FINEMET alloy $Fe_{74.5}Cu_1Nb_3Si_{13.5}B_9$). Samples for magnetocaloric experiments can be prepared either by quenching without external magnetic field, in which case the directions of the easy axis of magnetic uniaxial anisotropy of nanocrystalline grains are randomly oriented through the sample, or the quenching is done in a magnetic field and such samples have all their magnetic moments in the direction of the external magnetic field.

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The magnetocaloric behavior is understood as a process where the energy is transferred between magnons and phonons. The exchange of heat with the surrounding is excluded - our sample is adiabatically isolated and the sum of entropy of magnons and entropy of phonons is constant.

$$S^{\text{mag}} + S^{\text{phon}} = \text{constant.} \tag{1}$$

The alteration of an external magnetic field could change the magnetic entropy and such change has to be compensated. The compensation is mostly done by the change of spin temperature and partly also by the change of entropy of phonons. The entropy of phonons is usually much smaller than the entropy of magnons, but we shall see, that in nanocrystalline materials there is a possibility that the entropy could be comparable to the magnetic part of entropy (calculated from magnon energies).

The dependence of energy of magnetic collective excitations on external magnetic field is crucial for magnetocaloric behavior. It decides about the numbers of quasiparticles. From this standpoint is the special situation in the neighborhood of phase transitions. We will use for the following discussion some data about the dependence of collective excitations energies on external magnetic field obtained in works where the author of this paper participated.

We studied (together with V.G.Baryachtar and V.Sobolev [2]) the field dependence of energies of magnetoelastic excitations of ferromagnetic uniaxial structure in the neighborhood of magnetic phase transition. We used simple model of magnetoelastic interactions and found for some phonons (or better quasiphonons) with the specific directions of k-vectors their energies drastically decline in the neighborhood of the magnetic phase transition defined in Fig. 2. The consequence should be the flow of energy from magnons to phonons and the spin temperature of magnetic system should decay.

The second supporting argument, which we will use for the discussion of magnetocaloric behavior of nanocrystalline samples, is from works of author together with G.Kozlowski, L. Biegala and I. Veltrusky [3,4].

We predicted a changes of sign of magnetocaloric effect ($\mathrm{d}T/\mathrm{d}H^{\text{ext}}$) in the neighborhood of magnetic phase transitions in ferrimagnetic materials. The fig.2. shows us two areas of the negative sign of magnetocaloric effect. The first bigger area is until the external magnetic field turns the magnetic moments antiparallel to its direction and the second smaller area of negative magnetocaloric effect is before the external field turns all magnetic moments in its direction.

3. The magnetoelastic excitations in an uniaxial ferromagnet in the neighborhood to the phase transition.

The chosen experimental situation is seen in the Fig. 1. The increasing external magnetic field is supposed to be perpendicular to the easy axis of uniaxial magnetic anisotropy. The hamiltonian is composed from three parts:

$$H = H^{\text{magnetic}} + H^{\text{magnetoelastic}} + H^{\text{elastic}} \tag{2}$$

$$H^{\text{magnetic}} = a(\mathrm{d}\mathbf{M}/\mathrm{dr})^2 + A\mathbf{M}^2 - \beta(\mathbf{M}.\mathbf{n})^2 - \mathbf{M}.\mathbf{H} \tag{3}$$

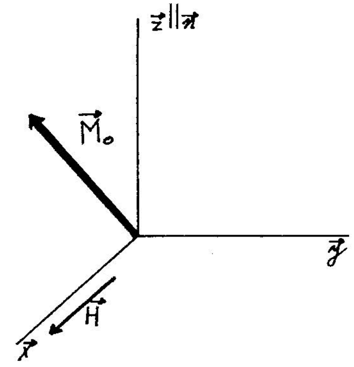

Fig.1

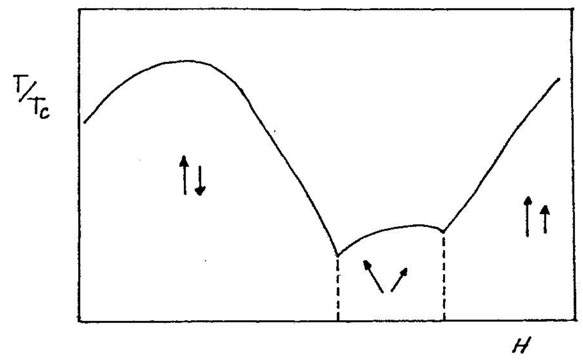

Fig. 2

a and A are constants of exchange term, β is the constant of anisotropy term, $\mathbf{n}$ is unit vector of anisotropy direction, $\mathbf{M}$ is density of magnetic moments, $\mathbf{H}$ is the external magnetic field,

$$H^{\text{magnetoelastic}} = gM_iM_ku_{ik} \tag{4}$$

g is magnetoelastic constant, u_{ij} is tensor of deformation, u is the deformation, $H^{elastic}$ contains terms proportional to $(u_{jj})^2$ and term proportional to u_{ij} .

The equilibrium values of components of tensor deformations and the equilibrium direction of magnetization were found and the standard method of approximate second quantisation gave us then the partly diagonal hamiltonian containing diagonal terms for magnons: $E_kc_k^\dagger c_k$, diagonal terms for phonons $E_kb_kb_k^\dagger$ but also non-diagonal terms $c_k^\dagger b_k$, $c_kb_k^\dagger$, $c_k^\dagger b_{-k}$ and c_kb_{-k}.

The transformation similar to Bogolubov transformation gave us the secular equation of 8th order for energies of quasiparticles corresponding to the collective excitations of our system (where the interaction between magnetic structure and elastic excitations of lattice were taken into account). The energies of all our new quasiparticles depend explicitly on the external magnetic field.

We were able to solve the secular equation analytically for the special directions of the wave vectors and the case of a weak magnon-phonon interaction. We supposed the appearance of two magnon-like energies with the quadratic dependence on the value of wave vector and six phonon-like magnetic field dependent energies, which are linearly dependent on the value of wave vector. Therefore the energies of quasiphonons are $\Omega^2 = (vk)^2$ ($\Omega_1 = \Omega_2 = c_\perp k$, $\Omega_3 = c_lk$. The index of speed c gives the orientation against wave vector $\mathbf{k}$). Suppositions: a)magnon-phonon interaction is weak: $\frac{\Delta l}{\beta} \ll 1$ ($\Delta l = \frac{(gM_0)^2}{2\rho c^2}$, c is a speed of sound, β anisotropy and ρ density).
b)small distance from phase transition point: $\Delta h \ll 1$ ($\Delta h =\mid \frac{H-H_c}{M_0} \mid$, H_c is the critical magnetic field).

$$v_{1,2} = \frac{1}{2}[c_t^2 + c_l^2 - \frac{\Delta l}{\Delta l + \Delta h}c_t^2(\kappa_x^2 + \kappa_z^2)]$$

$$\pm[\frac{1}{4}[c_t^2c_l^2-\frac{\Delta l}{\Delta l+\Delta h}c_l^2(\kappa_x^2+\kappa_z^2+c_t^2c_l^2[\frac{\Delta l}{\Delta l+\Delta h}(\kappa_x^2+\kappa_z^2)-\frac{4\Delta l}{\Delta l+\Delta h}c_t^2(c_t^2-c_l^2)(\kappa_x^2\kappa_z^2)]]^{1/2}$$

$$c_l^2=(\lambda+2\mu)/\rho;c_t^2=\mu/\rho \tag{5}$$

where $\kappa = \mathbf{k}/(|\ \mathbf{k}\ |)$, which gives in the phase transition ($\Delta h = 0$) zero energy for directions κ parallel x and κ parallel z.

Solution for a quasimagnons:

$$\Omega^2=\epsilon_k^2+\frac{\Delta l c_\perp}{(\Delta l+\Delta h)\epsilon_0}(k_x^2+k_z^2) \tag{6}$$

here is no zero at the point of phase transition. The flow of energy goes from magnons to phonons.

For the vicinity of phase transition (fig.1.) the energies of our quasimagnons are non-zero but the energies of some quasiphonons go to zero (for wave vectors parallel and perpendicular to the easy magnetocrystalline axis). The strong decay of quasiparticle energies could have important consequences for the thermodynamic behavior in the increasing external magnetic field.

4. Results and conclusions.

Let us turn to the main topic of this paper, to the discussion of magnetocaloric effect in nanocrystalline materials. We considered an amorphous magnetic medium with small nanocrystals embedded in it. The nanocrystals are big enough to contain their own collective excitations. The structure of nanocrystals is ferromagnetic with uniaxial magnetic anisotropy. The method of preparation of samples decide if axes of anisotropy are randomly distributed or ferromagnetically oriented in one direction.

Let us consider the case, that all magnetic moments in the sample are parallel and the sample is placed into the experimental apparatus so, that external field is perpendicular to magnetic moments. The increase of external magnetic field to some critical value will bring magnetic moments of all nanocrystalline grains parallel to external magnetic field. This is the situation of phase transition where we expect strong decay of energies of some quasiphonons. In the vicinity of critical magnetic field can be expected a flow of energy from magnetic excitations to elastic excitations - the decrease of spin temperature with increasing magnetic field.

The magnetocaloric experiment with a samples prepared by quenching without external magnetic field (random orientations of magnetocrystalline easy axises) should have enlarged the area of external magnetic fields for which the energy is flowing from magnons to phonons.

The numerical calculations of magnetocaloric behavior based on the model discussed in this paper are in progress for the special materials and will be published in further publication.

5. Remark about the possibility of superferromagnetic behavior of magnetic nanocrystalline materials.

In nanocrystalline magnetic material we have giant local moments. Grains can be considered as localized giant magnetic moments. They could have its own collective excitations [5].

The character of interactions between giant localized magnetic moments of nanocrystalline grains is not clear. One possibility is the magnetic dipol-dipol interaction, but one can think also about some kind of superexchange interaction. About an important role of magnetic dip-dip interaction spoke for example J. Planes and A. Finel [6].

The supporting argument for the existence of an important interaction between nanocrystalline grains is given by the experiments [1] which gave two very different critical magnetic temperatures T_{C1} and T_{C2} (for $Fe_{74.5}Cu_1Nb_3Si_{13.5}B_9$ are $T_{C1} = 321°C$, $T_{C2} = 600°C$).

If so, then the magnetic nanocrystalline materials could be an example of localized magnetic moments really existing in nature.

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