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Magnetocaloric effect and a first order spin-reorientation phase transition in cubic $HoAl_2$ compound.

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Abstract

A semiempirical thermodynamical approach was utilized to explore a phase diagram of the $HoAl_2$ intermetallic compound and give a qualitative description of the magnetic and magnetocaloric properties in the vicinity of the spin-reorientation phase transition. It was established that spontaneous spin reorientation from <110> to <100> direction is a first order phase transition. The estimated jump of entropy is ΔS=0.38 J/molK (10.4 mJ/cm^{3}K) and the latent heat ΔQ=7.6 J/mol. On the contrary, field induced spin reorientation is a second order phase transition. It was also demonstrated that the form of temperature dependence of the magnetocaloric effect measured previously for this sample is in the agreement with the predictions of semiempirical thermodynamical model.

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One of the important reasons behind the investigation of the magnetocaloric effect (MCE) in the solids is a development of the materials which could be used as working bodies of the magnetic refrigerators. Large values of MCE were found in the compounds where the first order phase transition is induced by external magnetic field. These achievements attracted more attention to the materials where the first order magnetic phase transitions take places. A lot of them were tested and comprehensive reviews of experimental results were published [1,2]. However the MCE values are usually calculated from results of magnetization or specific heat measurements and their relation to other characteristics of the material aren't established.

More information about magnetocaloric properties of the system can be obtained on the basis of the explicit expression for a free energy. Generally the calculation of a thermodynamical potential is a complicated task. But fortunately the semiempirical expression for a free energy can be developed taking into account the symmetry of the system. This method was used to calculate the adiabatic temperature change arising from fast rotation of single-crystalline nickel in magnetic

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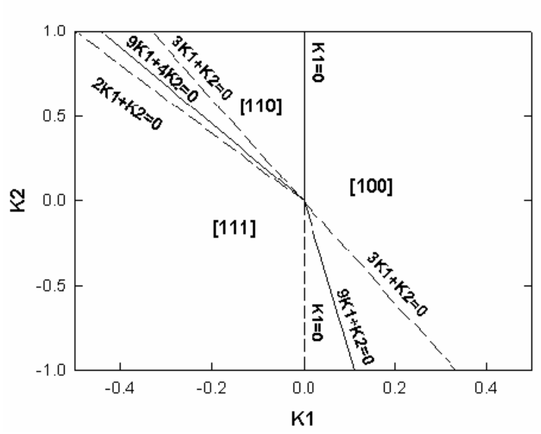

Fig. 1 The phase diagram of a cubic magnetic single crystal in the absence of magnetic field [12]. Solid lines are lines of phase transitions. Dashed lines are the border of the regions where two phases coexist.

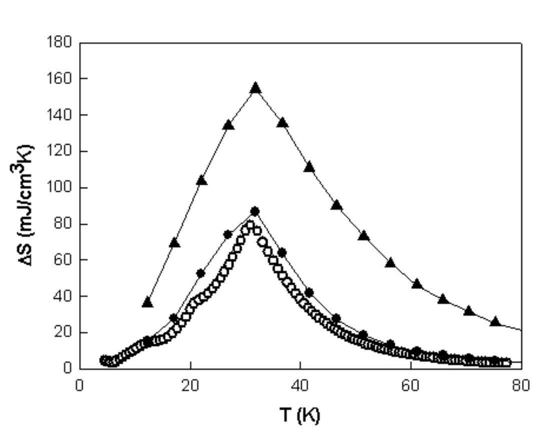

Fig. 2 Isothermal entropy change in $HoAl_2$ for the magnetic field changes of 2 T (circles) and 5 T (triangles). Open symbols – MCE calculated from results of heat capacity measurements. Closed symbols – MCE calculated from results of magnetization measurements [6].

field [3].

In the present work we utilize a semiempirical thermodynamical approach to calculate the value of MCE in the $HoAl_2$ intermetallic compound that undergoes a first order spin-reorientation phase transition. As far as authors know this is a first time when the values of the MCE arising from a first order spin-reorientation phase transition are calculated on
the basis of this technique.

$HoAl_2$ is a member of series RAl_2 intermetallic compounds which crystallize in the simple crystal structure $MgCu_2$ type, space group Fd3m. The rare earth ions belong to a diamond lattice and have equivalent sites of cubic point symmetry [4]. A simple ferromagnetic structure of $HoAl_2$ in the ordered state had been confirmed by the elastic neutron-scattering experiments [5]. The Curie temperature was observed in the range from 28 to 33 K [6-8]. The easy direction of magnetization is along <100> and below of the 20 K it turns to be along <110> [8-10]. The spontaneous spin reorientation is a first order phase transition [6-8]. Torque measurements have been performed on single crystal specimens by different authors but the kind of phase transition in the presence of magnetic field was a matter of discussion [9,10]. The $HoAl_2$ compound also has been experimentally studied with respect to its magnetocaloric properties [6,7,11].

Thermodynamical model for magnetic single crystal of cubic point symmetry had been developed in [12,13]. It was shown that in the absence of the magnetic field the free energy is

$$F = (1/4)[K_1 \sin^2 2\theta + \sin^2 2\phi \sin^4 \theta (K_1 + K_2 \cos^2 \theta)] \quad (1)$$

where K_1, K_2 are anisotropy constants and θ, ϕ are polar and azimuthal angles of magnetization vector with respect to the three cube edges. Three possible directions of magnetization, found by minimizing of (1), are <100>, <110>, <111>. The reorientation among two of these directions is a first order phase transition [12]. The phase diagram of the system is shown in the fig 1. In the presence of magnetic field the free energy is given by

$$F = |K_2| \{(1/4)\, q \sin^2 2\theta + (1/4)[q + K_2/|K_2|) \cos^2 \theta] * \sin^2 2\phi \sin^4 \theta - h[\sin\theta \sin\theta_h \cos(\phi - \phi_h) + \cos\theta \cos\theta_h]\} \quad (2)$$

where θ_h, ϕ_h are polar and azimuthal angles of magnetic field and

$$h = IH/|K_2|,$$
$$q = K_1/|K_2|.$$

It is implied that magnetization I is a field independent. The direction of magnetization could

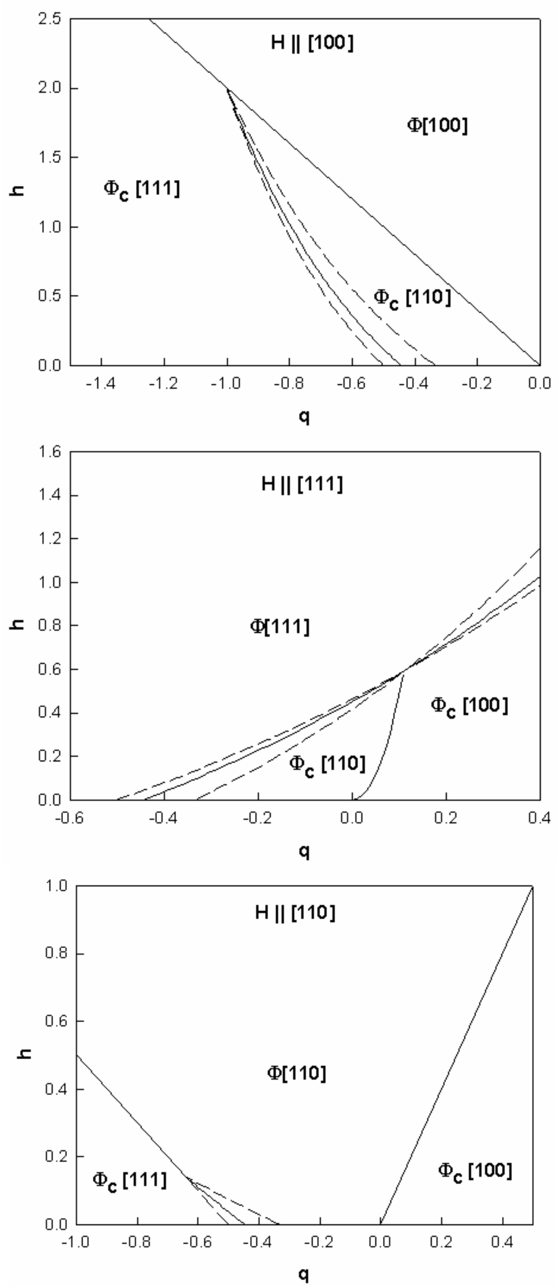

Fig. 3 The phase diagram of a cubic magnetic single crystal in the magnetic field directed along <100> (a), <111> (b) and <110> (c) crystallographic axes [13] found by minimizing (2). The type of phase diagram depends on the sign of K_2 and direction of the magnetic field [13].

be found by minimizing (2). The type of phase diagram depends on the sign of K_2 and direction of the magnetic field [13].

We start our analysis from the phase diagram shown in fig 1. The model (1) predicts that in the absence of the magnetic field spontaneous reorientation of the magnetization at 20 K is a first order phase transition. But it was also shown that the higher order anisotropy constant K_3 has to be taken into account to find out the type of the phase transition more precisely [12]. Unfortunately the third anisotropy constant K_3 isn't published still. However the sharp peak found on the temperature dependence of the heat capacity in the vicinity of 20 K is a characteristic feature of the first order phase transition [6,7]. From equation (1) we have free energy of <100> and <110> phases

$$F_{<100>} = 0, \quad F_{<110>} = K_1/4 \tag{3}$$

Since entropy is given by

$$S = -dF/dT \tag{4}$$

The discontinuous change of entropy ΔS due to a first order phase transition is

$$\Delta S = \tfrac{1}{4}\, dK_1/dT \tag{5}$$

Taking the value of derivation from [14] we have ΔS=0.38 J/molK (10.4 mJ/cm^{3}K) and then the latent heat ΔQ=7.6 J/mol. The experimental one is ΔQ=2.3 J/mol [7]. It is in a reasonable agreement with above estimation.

The isothermal entropy change calculated from results of the magnetization and specific heat measurements [6] shown in the fig 2. The curves of temperature dependence of the MCE are rather smooth and don't exhibit any sharp anomalies. We established that spontaneous reorientation of the magnetization at 20 K is a first order phase transition but we can't see contribution from latent heat to the values of magnetocaloric effect. To understand this phenomenon we have to examine the phase diagrams developed on the basis of the equation (2).

It is known that the first anisotropy constant K_1 is positive above 20 K and negative below this temperature [14]. Unfortunately the second anisotropy constant K_2 is not published still. But it is clearly seen that K_2 is positive below 20 K because easy direction of magnetization is along <110> in this temperature range. Above 20 K it can be deduced from torque measurements in (110) plane [15]. Our calculations show that K_2 is also positive at least up to 21.8 K.

The phase diagrams from [13] for $K_2>0$ and magnetic field directed parallel to <100>, <111> and <110> axes shown in fig 3 a, b and c. The subscript c at a phase title means that the phase is canted. The reorientation from canted <110> to <100> in the magnetic field directed parallel to <100> (fig 3a) and from canted <100> to <110> in the magnetic field directed parallel to <110> (fig 3c) is a second order phase transition [13]. This is in the agreement with conclusion of the paper [10] that in the presence of magnetic field spin reorientation from <100> to <110> direction in the (100) plane takes place continuously over a finite temperature range. The reorientation from canted <100> to canted <110> in the magnetic field directed parallel to <111> (fig3 b) can be a first or second order phase transition depending on higher order K_3 anisotropy constant [13].

Eventually the field induced spin reorientation of magnetization from <110> to <100> direction in $HoAl_2$ is most probably a second order phase transition. It isn't accompanied with release of latent heat. Then it doesn't have to give rise to discontinuous change of entropy and sharp anomalies on the curves of temperature dependence of the MCE.

In conclusion, a semiempirical thermodynamical approach was utilized to explore a phase diagram of the $HoAl_2$ intermetallic compound. It was established that spontaneous spin reorientation from <110> to <100> direction is a first order phase transition. The estimated jump of entropy is $\Delta S=0.38$ J/molK (10.4 mJ/cm^{3}K) and the latent heat $\Delta Q=7.6$ J/mol. That is in the reasonable agreement with the experimental one $\Delta Q=2.3$ J/mol. On the contrary, field induced spin reorientation is a second order phase transition. That is in the agreement with the results of some torque and MCE measurements. It was also demonstrated that semiempirical thermodynamical approach is useful in description of magnetocaloric properties of solids.

Acknowledgements

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