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Thermodynamic model of a solid with RKKY interaction and magnetoelastic coupling

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ABSTRACT

Thermodynamic description of a model system with magnetoelastic coupling is presented. The elastic, vibrational, electronic and magnetic energy contributions are taken into account. The long-range RKKY interaction is considered together with the nearest-neighbour direct exchange. The generalized Gibbs potential and the set of equations of state are derived, from which all thermodynamic functions are self-consistently obtained. Thermodynamic properties are calculated numerically for FCC structure for arbitrary external pressure, magnetic field and temperature, and widely discussed. In particular, for some parameters of interaction potential and electron concentration corresponding to antiferromagnetic phase, the existence of negative thermal expansion coefficient is predicted.

1. Introduction

Thermodynamics of solids with magnetoelastic couplings is a subject of extensive interest of solid state physicists since many years in its various aspects [1–41]. The magnetoelastic interactions are responsible for such effects as the magnetostriction [33,34,36] and piezomagnetism, which are important from the point of view of application. As another direct consequence of the presence of magnetoelastic coupling, one can mention the pressure influence on the magnetic phase transition temperature, which has been discussed in numerous works [2,17,24–27,32,42,43]. The studies involve both model systems and specific materials, among which a particularly important class of magnetic semiconductors can be mentioned [44–51]. Moreover, the contemporarily studied magneto-caloric materials also essentially rely on the existence of the coupling between the crystalline lattice and the magnetic subsystem [28,30,42,43,52], which influences the vital parameters of these materials.

In a common approach, the magnetoelastic coupling arises from the fact that the magnetic exchange integral between magnetic moments depends on their mutual distance [1,5–8,13,15,16,21,22,27,46,31,40,41,53], which makes the magnetic energy volume-dependent. On the other hand, the volume is an indispensable parameter occurring in other, non-magnetic, parts of the total energy, as for instance, the elastic potential energy, vibrational energy, as well as the electronic one.

For the system in stable equilibrium, the total energy must take the minimum value. This can be achieved when the volume and magnetization of the system are treated as variational parameters, whereas the external pressure, magnetic field and temperature are independent and fixed variables. The variational approach leads to the set of equations of state in which the volume and magnetization are interrelated and determined by the rest of independent variables. Thus, the influence of the external pressure on the magnetic variational parameter (magnetization) can be manifested, in addition to the expected change of the volume. On the other hand, the external magnetic field influences, via magnetic energy, the volume of the system, in addition to the expected change of the magnetization.

In our previous papers [40,41], the thermodynamic model for the magnetoelastic couplings was presented, for the simplest case

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when the magnetic interaction between localized spins was of Heisenberg type. The energy of itinerant electrons was not considered in that approach, thus restricting the model to magnetic insulators. However, the energy of electron subsystem is important in such systems as metals, being responsible for the metallic bonds and contributing to the elastic properties. On the other hand, the presence of electron gas enables the long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) indirect interaction between localized spins [54–56]. The exchange interaction in RKKY model is oscillating vs. distance, and its amplitude is volume-dependent. Thus, in a natural way it is sensitive to the volume deformation.

Since up to now studies of magnetoelastic properties with RKKY interaction included seem to be rather unexploited area, the aim of the present paper is to fill the existing gap. We will make use of the underlying methodology developed in our previous paper [40], and extend the approach by taking into account the itinerant electron energy in Hartree-Fock approximation. Then, the long-range RKKY interaction will be included in addition to the nearest-neighbour (NN) direct Heisenberg interaction. Thus, in the present model the magnetoelastic couplings have two sources: the volume dependence of the NN Heisenberg exchange integral, as well as the long-range RKKY interaction. In addition, when the external magnetic field is present, the effective gyromagnetic factor in the RKKY Hamiltonian occurs to be volume-dependent [57]. In our opinion, all these features make the present model interesting enough and much more complete than in the previous approach [40], since all essential energy contributions to the total Gibbs energy are now taken into account.

The paper is organized as follows: in the next, theoretical, section the formalism will be presented. It contains a self-consistent thermodynamic methodology developed for the complex systems with many variables, including derivation of the generalized Gibbs potential and the equations of state. Some complementary formulas are placed in the Appendix. In the third section the exemplary numerical results will be presented in figures and discussed. They concern calculation of various thermodynamic parameters in the presence of magnetoelastic coupling. The calculations are performed for a model FCC lattice with NN and RKKY interaction. A comparison of the results for different electron concentrations, which correspond to the existence of ferromagnetic or antiferromagnetic phases, is made there. In the last section, the paper will be summarized and the conclusions will be drawn.

2. Theoretical model

The Gibbs free energy of a system is assumed in the form of:

$$G = F_\varepsilon + F_{\mathrm{D}} + F_{\mathrm{el}} + pV + G_m, \tag{1}$$

where F_ε is the elastic (static) Helmholtz energy, F_{D} is the vibrational (thermal) Helmholtz energy in the Debye approximation, F_{el} is the electronic Helmholtz energy in the Hartree-Fock approximation, p is the external pressure, V-volume of the system, and G_m is the Gibbs energy of magnetic subsystem with RKKY interaction. These energy components will be presented below.

2.1. The elastic (static) subsystem

The elastic energy F_ε can be found on the basis of the Morse potential [58–60]. Considering the atomic pairs, where one atom stays in the centre of the system of coordinates and the second atom is situated on the k-th coordination sphere of radius r_k, the potential energy is given by:

$$U(r_k) = D\left(1 - e^{-\alpha(r_k - r_0)/r_0}\right)^2. \tag{2}$$

The pair-potential contains three fitting parameters: potential depth D, dimensionless asymmetry parameter α and the distance r_0 where the potential has its minimum.

We will assume that for the crystals with cubic symmetry the radius of k-th coordination sphere, r_k, can be expressed in terms of the isotropic volume deformation ε, namely:

$$r_k = r_{k,0}(1+\varepsilon)^{1/3}, \tag{3}$$

where $r_{k,0}$ is the radius of a non-deformed sphere and the isotropic volume deformation ε is defined by the equation:

$$V = V_0(1+\varepsilon) = \frac{N}{z_0} a_0^3 (1+\varepsilon). \tag{4}$$

In Eq. (4), $V_0 = V(p=0, H^z=0, T=0)$ is the volume of a non-deformed system (NDS) for $\varepsilon = 0$, which is assumed at pressure $p = 0$, magnetic field $H^z = 0$ and temperature $T = 0$. In the same formula, N is the number of atomic sites, z_0 stands for the number of atoms per elementary cell, and the lattice constant of a non-deformed cubic cell is denoted by a_0.

It is convenient to use the pair-potential energy after shifting it by a constant value, $U(r_{k,0})$, in order to set zero Helmholtz energy $F_\varepsilon(\varepsilon = 0) = 0$ for a non-deformed crystal. The total elastic energy can be written as a sum over all the interacting pairs. For isotropic system the sum can be conveniently performed over the coordination zones with radii $r_{k,0}$ and the coordination numbers z_k. Finally, the elastic energy can be presented in the form of [40]

$$F_\varepsilon = \frac{N}{2} D \times \sum_k z_k \left\{ \left[1 - e^{-\alpha\left(x\frac{r_{1,0}}{r_0}\frac{r_{k,0}}{a_0}(1+\varepsilon)^{1/3} - 1\right)} \right]^2 - \left[1 - e^{-\alpha\left(x\frac{r_{1,0}}{r_0}\frac{r_{k,0}}{a_0} - 1\right)} \right]^2 \right\}, \tag{5}$$

where the nearest neighbour normalized distance, $r_{1,0}/r_0$, can be found from the minimum conditions for the total Gibbs energy of a non-deformed crystal, whereas $r_{k,0}/a_0$ ratios and the coordination numbers z_k are characteristic of a given crystallographic structure and can be found numerically. We have also introduced the coefficient x relating the lattice constant and NN distance of a non-deformed lattice, namely $a_0 = x r_{1,0}$. This coefficient is characteristic of a given lattice. For instance, for FCC structure $x = \sqrt{2}$, whereas $z_0 = 4$. Thus, the expression (5) presents elastic energy for arbitrary isotropic deformation ε with the assumption that $F_\varepsilon(\varepsilon = 0) = 0$.

The change of the elastic energy vs. volume is a source of elastic pressure:

$$p_\varepsilon = -\left(\frac{\partial F_\varepsilon}{\partial V}\right)_T = -\frac{1}{V_0}\left(\frac{\partial F_\varepsilon}{\partial \varepsilon}\right)_T = -\frac{x}{3}\frac{N}{V_0} D\alpha \frac{r_{1,0}}{r_0} \sum_{k=1} z_k \times \frac{r_{k,0}}{a_0}\left[1 - e^{-\alpha\left(x\frac{r_{1,0}}{r_0}\frac{r_{k,0}}{a_0}(1+\varepsilon)^{1/3} - 1\right)} \right] \frac{e^{-\alpha\left(x\frac{r_{1,0}}{r_0}\frac{r_{k,0}}{a_0}(1+\varepsilon)^{1/3} - 1\right)}}{(1+\varepsilon)^{2/3}}. \tag{6}$$

This pressure should be taken into account together with other pressure contributions keeping the system in equilibrium.

2.2. The vibrational (Debye) subsystem

The vibrational energy is taken in the Debye approximation and for the arbitrary temperature T can be presented as [61]

$$F_{\mathrm{D}} = N\left[\frac{9}{8} k_{\mathrm{B}} T_{\mathrm{D}} + 3k_{\mathrm{B}} T \ln\left(1 - e^{-y_{\mathrm{D}}}\right) - 3k_{\mathrm{B}} T \frac{1}{y_{\mathrm{D}}^3} \int_0^{y_{\mathrm{D}}} \frac{y^3}{e^y - 1} dy\right], \tag{7}$$

where $y_{\mathrm{D}} = T_{\mathrm{D}}/T$ and T_{D} is the Debye temperature.

The Debye temperature is volume-dependent and can be expressed in the approximate form [62]