ISSN 1063-7834, Physics of the Solid State, 2018, Vol. 60, No. 6, pp. 1177–1179. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © S.G. Ovchinnikov, Yu.S. Orlov, S.V. Nikolaev, A.I. Nesterov, T.M. Ovchinnikova, 2018, published in Fizika Tverdogo Tela, 2018, Vol. 60, No. 6, pp. 1166–1168.

PHASE TRANSITIONS

Effect of the Interatomic Exchange Interaction on the Magnetic Phase Transitions in Spin Crossover Systems under High-Pressure

S. G. Ovchinnikov[a, b], Yu. S. Orlov[a, b, *], S. V. Nikolaev[a, b], A. I. Nesterov[c], and T. M. Ovchinnikova[d]

[a] *Siberian Federal University, Krasnoyarsk, 660041 Russia*

[b] *Kirensky Institute of Physics, Krasnoyarsk Scientific Center, Russian Academy of Sciences, Siberian Branch, Krasnoyarsk, 660036 Russia*

[c] *Guadalajara University, Department of Physics, Guadalajara, 44100 Mexico*

[d] *Sukachev Institute of Forest, Krasnoyarsk Scientific Center, Russian Academy of Sciences, Siberian Branch, Krasnoyarsk, 660036 Russia*

**e-mail: jso.krasn@mail.ru*

Received December 11, 2017

Abstract—The phase diagram of an antiferromagnet with the spin crossover from the high-spin to low-spin state with $S = 0$ with increasing external pressure has been calculated with regard to the pressure dependence of the exchange integral. The calculated results are compared with the experimental data on ferropericlase $Fe_xMg_{1-x}O$.

DOI: 10.1134/S1063783418060276

1. INTRODUCTION

The spin crossovers in magnetic dielectrics are observed in many iron oxides in experiments with diamond anvils under a typical critical pressure of P_c = 50–70 GPa [1]. The magnetic state of an iron ion is usually detected using the Mössbauer effect. The change of the high-spin (HS) state for low-spin (LS) one can also be observed using X-ray spectra, which is especially convenient for samples in the paramagnetic phase. In addition, the pressure dependence of the substance volume is sensitive to the spin state, since the ionic radius of the LS ion is significantly (by about 10%) smaller than the radius of the HS ion. The conventional theoretical description of the spin crossovers is based on the single-ion pattern, where the HS state is stabilized by the Hund interatomic exchange integral and the LS state is stabilized by the crystal field, which increases with the pressure. Therefore, the HS state typical of an isolated atom is changed for the LS state, when the crystal field energy becomes equal to the Hund exchange. In such a pattern, the zero-temperature spin crossover is a quantum phase transition with respect to pressure with the topological order parameter [2], while at finite temperature, the phase transition does not occur and the spin crossover represents a smooth transition from one state to the other. The question whether the spin crossover is a thermodynamic phase transition is still unanswered. The experimental study of spin crossovers in a wide class of magnetic oxides sometimes, yet not always, reveals a volume jump at the crossover [1].

In this study, we analyze the effect of interatomic exchange coupling on the spin crossover. We investigated the model with the LS term $S = 0$, which corresponds to the d^6 compounds, e.g., ferropericlase $Fe_xMg_{1-x}O$. Using the mean-field approximation, we demonstrate the occurrence of a series of first-order phase transitions from the antiferromagnetic HS state to the nonmagnetic LS state with respect to pressure near the temperature-dependent critical pressure in the magnetic phase diagram on the (T, P) plane with regard to the interatomic exchange [3]. Such behavior is observed at temperatures below the tricritical point $T^* < T_N$. Above the tricritical point, the pressure transition with be second-order. Above the Néel point, the spin crossover, as in the absence of the interatomic exchange, consists in the smooth transition from one state to the order. The low-pressure Néel temperature linearly increases with the interatomic exchange coupling.

2. EFFECTIVE HAMILTONIAN IN THE MEAN-FIELD APPROXIMATION

In compounds with the spin crossover, the state of a system is specified by the spin and orbital quantum numbers. Near the spin crossover, only the two states, HS and LS, are important, which can be distinguished

by the pseudospin $\tau_z = +1/2$ and $\tau_z = -1/2$. The microscopic derivation of the effective Hamiltonian describing the possibility of spin crossover and magnetic order by means of the interatomic exchange (spin ordering) has been recently made by us using the multi-electron LDA + GTB (local density approximation plus generalized tight-binding) approach [4].

In the case of d^6 ions with $S_{HS} = 2$ and $S_{LS} = 0$ S, the effective Hamiltonian [4] in the mean-field approximation for the spin and pseudospin variables in the antiferromagnetic phase has the form

$$H = H_0 - \sum_i \mathbf{B}\mathbf{S}_i - \Delta_{\text{eff}} \sum_i \tau_i^z. \quad (1)$$

Here, $\mathbf{B} = zJSn^2 \langle \mathbf{m} \rangle$ is the two-sublattice mean field, $\mathbf{S}_i$ and τ_i^z are the spin and pseudospin operators on the ith crystal lattice site, and $\tau_i^z |\alpha\rangle = \lambda_\alpha |\alpha\rangle$. Index α takes the values 1 and 2 for the HS and LS states, respectively. The eigenvalues λ_α are $\lambda_1 = 1$ and $\lambda_2 = -1$. $\langle \mathbf{m} \rangle = (0, 0, m)$ is the mean value of the magnetization vector $\langle \mathbf{S}_i \rangle = S \langle \mathbf{m}_i \rangle$,

$$H_0 = \frac{Nvm^2}{2} n(3n-1) - \frac{Nv}{2} n(1-n), \quad (2)$$

and

$$\Delta_{\text{eff}} = \frac{v}{2}(1+m^2)n + \varepsilon_0 - f(P), \quad (3)$$

where $v = zJS^2$, z is the number of nearest neighbors, $g = g_{HS}/g_{LS}$ is the ratio between the HS and LS state degeneracy multiplicities ($g = 15$ for Fe^{2+} ions), β is the reciprocal temperature, n is the population of the HS state, N is the number of lattice sites, and $\varepsilon_0 = \Delta_S/2$ ($\Delta_S = E_{LS} - E_{HS}$ is the spin gap, i.e., the energy interval between the LS and HS states at zero pressure). Hereinafter, we assume the pressure dependence of the crystal field to be linear, $f(P) = aP$ (the crossover point $P = P_C$ is determined by the condition $\varepsilon_0 = f(P_C)$) and the pressure dependence of the exchange integral $J(P) = J_0 + bP$ to be linear, as well [5]. The self-consistency equations for the sublattice magnetization m and occupation numbers n, which determine the mean value of the pseudospin, have the form

$$m = B_S(\beta v m n^2) \quad (4)$$

and

$$n = \frac{1 + \tanh(\beta\Delta_{\text{eff}}(P) + \ln\sqrt{g})}{2}, \quad (5)$$

where $B_S(x)$ is the Brillouin function.

3. P–T PHASE DIAGRAM

First, we consider the solution of Eqs. (4) and (5) at zero exchange coupling ($J = 0$). In this case, we have $m = 0$ for the magnetization and the sharp jump of the HS state population at the crossover point at $T = 0$, which corresponds to the quantum phase transition [2]. At $J = 0$, the quantum phase transition with increasing temperature is spread to the smooth crossover. We solved Eqs. (4) and (5) numerically, taking into account the exchange coupling. At specified temperatures and pressures, there can be several solutions for the parameters m and n; among these solutions, we choose those corresponding to the minimum Helmholtz free energy

$$F = H_0/N - k_B T \ln Z_S - k_B T \ln Z_\tau,$$

where

$$Z_S = \frac{\sinh\left(\left(1 + \frac{1}{2S}\right)\beta v m n^2\right)}{\sinh\left(\frac{1}{2S}\beta v m n^2\right)}$$

and

$$Z_\tau = 2\sqrt{g}\cosh(\beta\Delta_{\text{eff}} + \ln\sqrt{g}).$$

The external pressure and temperature are given in units P_C and exchange coupling J_0, respectively. Hereinafter, the calculations were made for the following set of parameters: $J_0 = 28$ K, $S = 2$, $z = 6$, $g = 15$, $a = 80$ K GPa^{-1}, $b = 0.5$ K GPa^{-1}, and $P_C = 55$ GPa.

Figure 1 shows diagrams of the HS state population n (Fig. 1a) and magnetization m (Fig. 1b), which are a self-consistent solution of the system of Eqs. (4) and (5). It can be seen that, due to the presence of the cooperative exchange coupling J, the system is retained in the ground magnetically ordered state up to $P_0 > P_C$, although in the single-ion pattern at $P > P_C$ the ground state is the nonmagnetic LS state. At $P > P_0$, the ground magnetic state changes for the nonmagnetic state via the first-order transition.

In the pressure range of $P \le P_0$ (Fig. 1b), the system undergoes the second-order phase transition to the paramagnetic state with increasing temperature. One can clearly see that the P–T diagrams contain a singularity (the so-called tricritical point, T^* and P^* in Fig. 1b), where the second-order phase transition line continuously passes to the first-order phase transition line. At $P_0 < P \le P'$, the ground state of the system is nonmagnetic, but, as the temperature increases, the magnetic HS state is populated and the system restores the energetically more favorable long-range magnetic order via the first-order phase transition (Fig. 1b). Thus, due to the cooperative interaction J, in systems with the spin crossover under pressure the return magnetization can exist. As the temperature further increases, the system passes to the paramagnetic state via the second-order phase transition at $P_0 < P \le P^*$ and via the first-order one at $P^* < P \le P'$. As the pressure increases, at $P > P_C$, the energy interval between the ground nonmagnetic LS state and the nearest excited magnetic HS state and at $P > P'$ (Fig. 1b), the

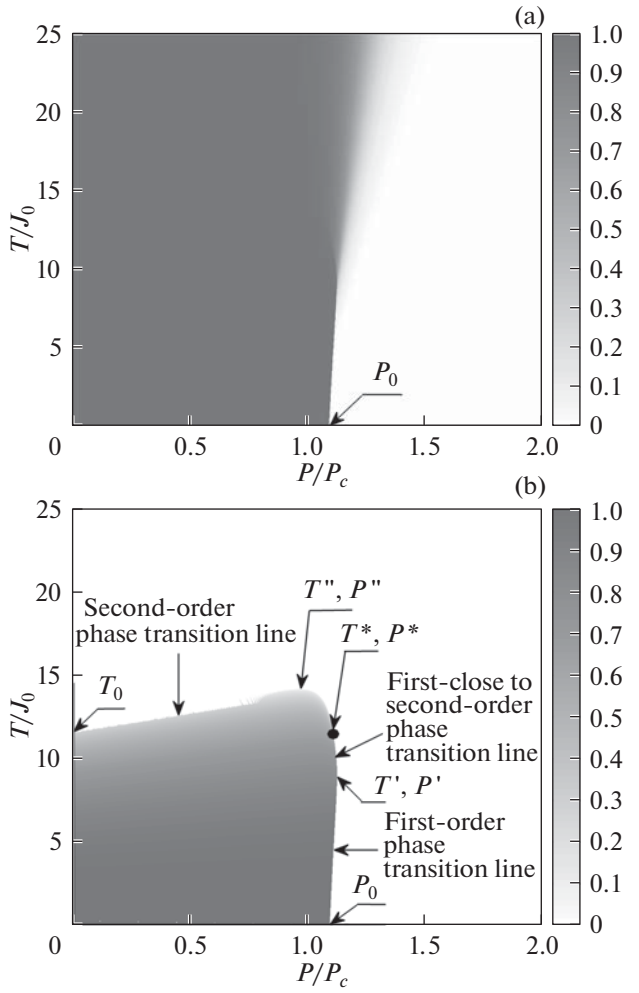

Fig. 1. Diagram of (a) the HS state population n and (b) magnetization m corresponding to the minimum free energy F.

heat energy required to populate the HS state in a desired degree becomes comparable with the exchange coupling J; the magnetic order does not occur.

Along with the existing return magnetization upon temperature variation at $P_0 < P \le P'$, taking into account the growth of exchange integral with pressure, the existence of the return magnetization upon pressure variation becomes possible at $T_0 < T \le T''$, where T_0 is the Néel temperature at $P = 0$ and T'' is the maximum possible Néel temperature with increasing pressure. In particular, at $T_0 < T \le T''$ (Fig. 1b), the system passes with increasing pressure from the paramagnetic state first to the magnetically ordered state via the second-order phase transition and then to the nonmagnetic state via the second-order phase transition at $T^* < T_0$ or either the first-order one at $T^* > T_0$ and $T_0 < T < T^*$ or the second-order one at $T^* > T_0$, but $T^* < T < T''$. For our set of parameters, we have $T^* < T_0$.

4. CONCLUSIONS

The exchange coupling near the spin crossover under pressure leads to the extraordinary rearrangement of a system. The magnetic ordering can be suppressed by the external pressure and the quantum phase transition is rearranged first to the first-order transition and then to the second-order one with increasing temperature. Due to the cooperative interatomic exchange coupling, in systems with the spin crossover under pressure the return magnetization upon temperature and pressure variation can exist under pressure.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, Government of the Krasnoyarsk Territory, and Krasnoyarsk Territorial Foundation for Support of Scientific and R&D Activities, projects nos. 16-42-243048 and 16-42-240413, the Grant Council of the President of the Russian Federation, project no. SP-1844.2016.1, and the Russian Foundation for Basic Research, projects nos. 16-02-00507, 16-02-00273, and 18-02-00453.

REFERENCES

1. I. S. Lyubutin and A. G. Gavrilyuk, Phys. Usp. **52**, 989 (2009).
2. A. I. Nesterov and S. G. Ovchinnikov, JETP Lett. **90**, 580 (2009).
3. Yu. S. Orlov, S. V. Nikolaev, A. I. Nesterov, and S. G. Ovchinnikov, JETP Lett. **105**, 771 (2017).
4. A. I. Nesterov, Yu. S. Orlov, S. V. Nikolaev, and S. G. Ovchinnikov, Phys. Rev. (in press).
5. I. S. Lyubutin and S. G. Ovchinnikov, J. Magn. Magn. Mater. **324**, 3538 (2012).

Translated by E. Bondareva