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# Magnetic and Structural Phase Transitions in Systems with Spin Crossover under Pressure

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The effect of the exchange interaction between excited high-spin terms of transition metal ions in magnetic Mott–Hubbard insulators on the thermodynamics of the system with singlet terms of ions in the ground state near the crossover of singlet and high-spin terms with the increase in the pressure is studied with the effective Hamiltonian. It is shown that the crossover at the temperature below the critical $T^* < T_N$ is a first-order phase transition and is accompanied by a volume jump. The crossover at the temperature above $T^*$ is accompanied by a smooth change in the crystal volume.

**1.** Spin crossovers at high pressures in transition metal oxides have been actively studied in recent times [1]. Concerning its nature, spin crossover is an effect consisting in the intersection of the magnetoelectric terms of $d^n$ configurations of magnetic ions with different spin values. According to [2], spin crossover is due to the competition of the intra-atomic Hund exchange interaction $J_H$ and the crystal field energy $10Dq$. A vivid manifestation of spin crossover is the change in the Mössbauer spectrum [3] and the optical absorption edge [4] in $FeBO_3$. The multielectron model of the electronic structure of $FeBO_3$ describing the spin crossover and the change in optical spectra was proposed in [5, 6]. Spin crossover was considered in magnesiowustite $Mg_{1-x}Fe_xO$ by the LDA+U method [7] and in FeO by the LDA+DMFT method within the band theory with allowance for local Coulomb correlations [8]. The effect of the interatomic exchange interaction on spin crossover is barely considered in the literature. Since it forms the magnetic ground state in magnetic insulators and provides cooperative properties of magnetic ions, it is of interest to reveal the effect of the interatomic exchange on spin crossover.

Two competing spin terms of the $d^n$ ion (we call them high-spin (HS) and low-spin (LS)) have different distributions of $n$ electrons over orbitals. Therefore, spin crossover is always associated with the orbital ordering. Unlike the orbital ordering in the Kugel'–Khomskii model [9], ordering in our case occurs for multielectron states having not only different total spins but also different orbital angular momenta. Nevertheless, only two states (HS and LS), which can be distinguished by the pseudospin $\tau^z = +1/2$ and $\tau^z = -1/2$, are essential near spin crossover. Recently, we derived microscopically the effective Hamiltonian describing the possibility of spin crossover (pseudospin ordering) and the magnetic order owing to the interatomic exchange (spin ordering) within the multielectron LDA+GTB method [10]. In this work, we show that, because of the interatomic exchange, spin crossover under pressure at low temperatures (in the region of the magnetic ordering) is a first-order isostructural phase transition. The interrelation of structural properties and spin crossover is due to different ion radii of HS and LS terms.

**2.** We limit ourselves to the case of $d^6$ ions (FeO and $Mg_{1-x}Fe_xO$), for which $S_{HS} = 2$ and $S_{LS} = 0$. The effective Hamiltonian [10] in the mean field approximation for spin and pseudospin variables in the antiferromagntic phase has the form

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

Here, $\mathbf{B} = zJSn^2 \langle \mathbf{m} \rangle$ is the two-sublattice mean field; $\mathbf{S}_i$ and $\tau_i^z$ are the spin and pseudospin operators at the $i$th site of the crystal lattice, respectively; and $\tau_i^z |\alpha\rangle = \lambda_\alpha |\alpha\rangle$. The index $\alpha$ takes the values 1 and 2 corresponding to the HS and LS states, respectively; the eigenvalues are $\lambda_1 = 1$ and $\lambda_2 = -1$; $\langle \mathbf{m} \rangle = (0, 0, m)$

is the average value of the magnetization vector $\langle \mathbf{S}_i \rangle = S \langle \mathbf{m}_i \rangle$;

$$H_0 = \frac{N\nu m^2}{2} n(3n-1) - \frac{N\nu}{2} n(1-n), \qquad (2)$$

$$\Delta_{\mathrm{eff}} = \frac{\nu}{2}\left(1+m^2\right)n + \varepsilon_0 - f(P). \qquad (3)$$

Here, $\nu = zJS^2$, $z$ is the number of nearest neighbors, $g = g_{\mathrm{HS}}/g_{\mathrm{LS}}$ is the ratio of degeneracy multiplicities of HS and LS states ($g = 15$ for ions $Fe^{2+}$), $\beta$ is the inverse temperature, $n$ is the population of HS states, $N$ is the number of lattice sites, and $\varepsilon_0 = \Delta_S/2$, where $\Delta_S = E_{\mathrm{HS}} - E_{\mathrm{LS}}$ is the size of the spin gap (the energy interval between LS and HS states) at zero pressure. Further, we assume the linear pressure dependence of the change in the crystal field: $f(P) = aP$; the crossover point $P = P_C$ is determined by the condition $\varepsilon_0 = f(P_C)$. Equations of self-consistency for the magnetization of the sublattice $m$ and filling numbers $n$ determining the average pseudospin value have the form

$$m = B_S\left(\beta\nu m n^2\right), \qquad (4)$$

$$n = \frac{1 + \tanh\left(\beta\Delta_{\mathrm{eff}}(P) + \ln\sqrt{g}\right)}{2}, \qquad (5)$$

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

To describe the change in the volume of the system at the change in the temperature and external pressure, we use the Birch–Murnaghan equation

$$\begin{aligned} P(V) = &\frac{3}{2}B_0\left[\left(\frac{V}{V_0}\right)^{-7/3} - \left(\frac{V}{V_0}\right)^{-5/3}\right] \\ &\times\left\{1 + \frac{3}{4}\left(B_0' - 4\right)\left[\left(\frac{V}{V_0}\right)^{-2/3} - 1\right]\right\}, \end{aligned} \qquad (6)$$

where $B_0$ is the bulk modulus, $B_0'$ is its pressure derivative (usually $B_0' = 4$), and $V_0$ is the volume of the unit cell at the normal pressure ($P = 0$). The volume of the unit cell as a function of pressure and temperature can be represented as

$$\begin{aligned} V(P,T) = &V_{\mathrm{HS}}(P,T)n(P,T) \\ &+ V_{\mathrm{LS}}(P,T)[1 - n(P,T)], \end{aligned} \qquad (7)$$

where $V_{\mathrm{HS}}(P,T)$ and $V_{\mathrm{LS}}(P,T)$ is the volume of the unit cell in the phase of the HS and LS states, respectively, and $n(P,T)$ is the population of the HS state determined by the system of equations (4), (5). In turn, $V_{\mathrm{HS}}(P,T)$ is determined from the equation

$$P(V) = \frac{3}{2}B_0^{\mathrm{HS}}\left[\left(\frac{V_{\mathrm{HS}}}{V_0^{\mathrm{HS}}}\right)^{-7/3} - \left(\frac{V_{\mathrm{HS}}}{V_0^{\mathrm{HS}}}\right)^{-5/3}\right], \qquad (8)$$

where $V_0^{\mathrm{HS}} = V_0^{\mathrm{HS}}(T) = V_0^{\mathrm{HS}}(0)(1 + \beta_{\mathrm{HS}}T)$, and $V_{\mathrm{LS}}(P,T)$ is found from the expression

$$P(V) = \frac{3}{2}B_0^{\mathrm{LS}}\left[\left(\frac{V_{\mathrm{LS}}}{V_0^{\mathrm{LS}}}\right)^{-7/3} - \left(\frac{V_{\mathrm{LS}}}{V_0^{\mathrm{LS}}}\right)^{-5/3}\right], \qquad (9)$$

where $V_0^{\mathrm{LS}} = V_0^{\mathrm{LS}}(T) = V_0^{\mathrm{LS}}(0)(1 + \beta_{\mathrm{LS}}T)$, and $B_0^{\mathrm{HS/LS}}$ and $\beta_{\mathrm{HS/LS}}$ are the bulk modulus and the volumetric thermal expansion coefficient, respectively, in the phase of the HS/LS state.

**3.** First, we consider solutions of the system of equations (4), (5) in the absence of the exchange interaction at $J = 0$. In this case, we have $m = 0$ for the magnetization and a sharp jump of the population of the HS state at the crossover point at $T = 0$ corresponding to the quantum phase transition [11]. At $J = 0$, the quantum phase transition with the increase in the temperature is smeared into a smooth crossover. Equations (4) and (5) were solved numerically with allowance for the exchange interaction. The appearance of several solutions is possible for the given temperature and pressure values for the parameters $n$ and $m$, from which we select those corresponding to the minimum of the thermodynamic Gibbs potential $G = F + PV$, where $F = E - TS$ is the Helmholtz free energy and $S$ and $V$ are the entropy and the volume of the system, respectively. The external pressure and temperature are given in units of $P_C$ and the exchange interaction $J$, respectively. Here and below, the calculations were carried out for the following parameters: $J = 28$ K, $S = 2$, $z = 6$, $g = 15$, $a = 80$ K/GPa, and $P_C = 55$ GPa. For parameters determining the cell volume, we used the values obtained earlier for $GdCoO_3$ crystals, where $Co^{3+}$ ions are in the same configuration $d^6$, and the spin crossover occurs with change in the temperature [12]: $B_0^{\mathrm{HS}} = 200$ GPa, $B_0^{\mathrm{LS}} = 250$ GPa, $\beta_{\mathrm{HS}} = 5\times10^{-7}$ $K^{-1}$, $\beta_{\mathrm{LS}} = 1\times10^{-7}$ $K^{-1}$, $V_0^{\mathrm{HS}} = 225.87$ Å$^3$, and $V_0^{\mathrm{LS}} = 209.35$ Å$^3$.

The left panels in Fig. 1 show all possible solutions of the system of equations (4), (5) denoted with red circles for the magnetization $m$ and with blue crosses for the population of the HS state $n$ as functions of the pressure for some temperature values $T$ (see below). In particular, a nonmagnetic solution $m = 0$ exists at all parameters. Solutions corresponding to the minimum of the thermodynamic Gibbs potential are joined by solid lines (red line for the magnetization $m$, blue line for the population of the HS state $n_{\mathrm{HS}}$). Other solutions have a metastable character. The right panels in Fig. 1 show the dependence of the volume of the unit cell on the external pressure $P$ calculated by Eq. (7). Similar to the left panels, the values of the volume corresponding to the minimum of the thermodynamic Gibbs potential are joined by the solid line.
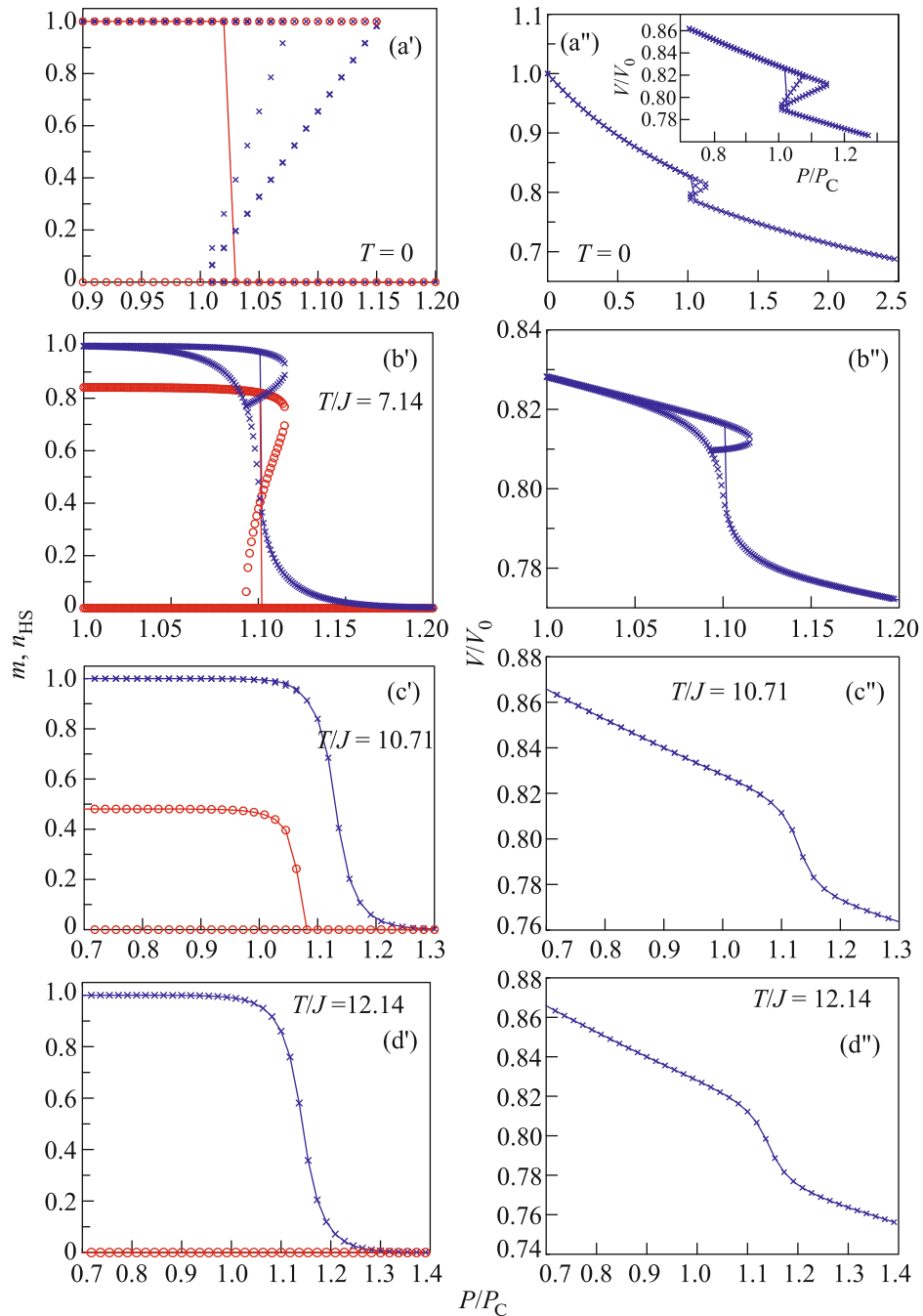
**Fig. 1.** (Color online) (Left panels) Solutions of the self-consistent system of equations (4) and (5) for different values of the temperature $T$ and (right panels) the volume of the unit cell (7) versus the external pressure $P$. Pairs of solutions for (circles) the magnetization $m$ and (crosses) the population of the HS state $n_{HS}$, for which the thermodynamic potential $G$ has the lowest value, are joined by the solid line.

It is seen well at $T = 0$ (see Fig. 1a') that the system undergoes a sharp transition from the magnetically ordered state to the nonmagnetic one, and the volume undergoes a jump (see Fig. 1a'') at the transition point. There is a region of metastable states of the system, which could lead to the appearance of the hysteresis. In the absence of the exchange interaction $J = 0$, the

abrupt change in the magnetic moment and the volume at $T = 0$ remains but the existence of metastable states becomes impossible.

With the increase in the temperature (see Fig. 1b'), the first-order phase transition is found at $0 < T \leq T^*$, and the region of metastable states decreases. The vol-
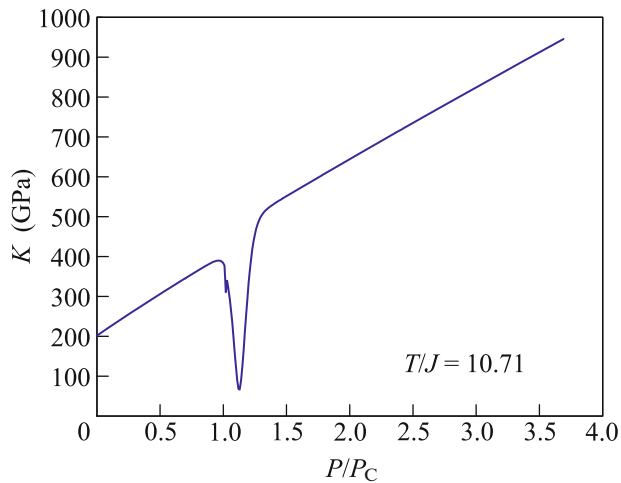
**Fig. 2.** Modulus of elasticity versus the external pressure at room temperature.

ume undergoes a jump at the transition point (Fig. 1b″). The critical temperature is $T^*/T_N = 0.8$. At $J = 0$ and an arbitrarily low temperature, the existence of the magnetization $m$ becomes impossible, and the volume undergoes a smooth transition (crossover).

At $T^* < T \leq T_N$ (see Fig. 1c′), we have a continuous second-order transition at the variation of the pressure again in accordance with the $P–T$ phase diagram. In this case, a smooth change in the volume is observed (see Fig. 1c″). It should be noted that the magnetic transition in this temperature range occurs a bit earlier than the structural one (see Fig. 1c′). In the paramagnetic phase, the concentration $n_{HS}$ changes smoothly with pressure (see Fig. 1d′), and the pressure dependence of the volume (see Fig. 1d″) is as smooth as that in Fig. 1c″.

Features in the behavior of the volume with the increase in the pressure lead to anomalies of the modulus of elasticity and the speed of sound. Figure 2 shows the pressure dependence of the modulus of elasticity at room temperature.

**4.** The exchange interaction near the spin crossover under pressure leads to unusual behavior of the system. The magnetic ordering can be suppressed by the external pressure, and the region of metastable states arises near the quantum critical point. The quantum phase transition with the increase in the temperature transforms first into a first-order transition and then into a second-order transition. The appearance of first-order phase transitions with discontinuities of the magnetic moment and the population of ion terms leads to the discontinuity of the crystal volume as a function of the temperature and pressure. Features in the behavior of the volume with the increase in the pressure lead to anomalies of the modulus of elasticity

and the speed of sound in systems with the spin crossover. Comparison of our results with experimental data on the change in the volume at the spin crossover in iron oxides from review [1] shows qualitative agreement. The pressure dependence of the volume in chambers with diamond anvils is usually measured at room temperature. Data for $FeBO_3$ and other oxides with the magnetic order at 300 K given in [1] show the hysteresis of the dependence $V(P)$, and the dependence $V(P)$ for $Mg_{1-x}Fe_xO$ with $T_N \sim 50$ K is smooth, similar to that in Fig. 1d″.

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