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Mechanisms of the Insulator–Metal Transition and Spin Crossover in CoO at High Pressure

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The effect of high pressure on the electronic characteristics of CoO is analyzed in the framework of the multi-electron model of transition metal oxides. The specific features of spin crossover for d^7 terms of Co^{2+} are compared to those characteristic of d^5 and d^6 configurations. A pressure-induced transition between antiferromagnetic and ferromagnetic states at the spin crossover point is predicted. A model is proposed to describe the pressure-induced variation of the electrical resistance exhibiting a stepwise change by eight orders of magnitude at the structural transition point observed at 43 GPa and the subsequent metallization above 133 GPa.

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1. The tendency toward metallization of insulators at megabar pressures is well known. In this way, recent spectacular advances have been achieved in obtaining high- T_c superconductivity in hydrides with the transition temperature above 200 K at pressures above 200 GPa [1–4]. This stimulates studies on the behavior of other materials, for example, iron hydrides at ultrahigh pressures [5], and on the metallization of molecular hydrogen [6]. Transition metal oxides, such as MnO, FeO, CoO, and NiO monoxides with the NaCl-type structure, are usually antiferromagnetic (AFM) Mott–Hubbard insulators at ambient pressure because of strong electron correlations. At high pressures, such materials can undergo insulator–metal transitions, which are due to the broadening of the electron band and spin crossovers from the high-spin (HS) to the low-spin (LS) state related to an increase in the crystal field [7–11]. In general, these two phenomena can be correlated [12].

In this work, we study spin crossover and metallization in CoO. Experimentally, at pressures up to 150 GPa, this material undergoes the following structural phase transitions: a transition from the cubic Cube I phase to the orthorhombic Rhom I phase at $P_{c1} = 43$ GPa without changing the volume, then the Rhom I–Rhom II transition at $P_{c2} \sim 90$ GPa with a change in volume by 2.7%, and, eventually, return to the cubic Cube II phase at $P_{c3} \sim 120$ GPa [13, 14]. The pressure dependence of the electrical resistance is characterized by a sharp decrease (a stepwise change

by eight orders of magnitude) in the pressure range of 43–63 GPa, a kink at 80 GPa, and the metallic behavior arising at 133 GPa [14]. The authors of [14] discuss the possibility of spin collapse in the range of 80–90 GPa, mainly referring to the calculations reported in [7]. In the current literature, we have not found any direct experimental evidence of spin crossover in CoO.

For this reason, we theoretically analyze the mechanisms of the insulator–metal transition and spin crossover, as well as their possible relationship in CoO, within the many-electron scheme [12, 15]. Earlier in [15], it was shown that, in general, spin crossover can change the effective electron correlation parameter, in particular, reducing it for d^5 configurations. The enhancement of correlation effects for d^6 configurations and the specific features of the pressure-induced insulator–metal transitions were considered in [12]. In this work, we show that spin crossover in the Co^{2+} ion in the d^7 configuration does not affect the electron correlation parameter and discuss possible mechanisms of the effect of pressure on the behavior of the electrical resistance.

2. It is well known that strong correlations split a one-electron band in the Hubbard model into the lower and upper Hubbard subbands. In the conventional Hubbard model with an orbitally nondegenerate band of width $2W$ and an intra-atomic Hubbard Coulomb parameter U , the band gap $E_g = U - W$ in the case of a half-filled band in the limit of strong electron

correlations ($U \gg W$) decreases with increasing pressure because of the band broadening $W(P) = W(0) + \alpha_W P$ when the interatomic distance decreases. This leads to the Mott–Hubbard insulator–metal transition, when the half-width of the band attains the critical value $W_c = aU$ ($a \sim 1$) [16, 17]. The Hubbard parameter U is of intra-atomic nature and is assumed to be pressure-independent.

The situation becomes different in multiorbital analogs of the Hubbard model, which can be used to describe $3d$ metal oxides with a predominantly ionic type of chemical bond. For such models, the initial Hubbard concepts should be supplemented by taking into account various multielectron d^n terms and anionic sp states. In the low-energy range, the effective Hamiltonian of such multiband p – d model can be written in the form of the effective Hubbard model, in which the d^0 , d^1 , and d^2 atomic terms of the single-band Hubbard model are replaced by local multielectron d^{n-1} , d^n , and d^{n+1} terms, respectively [18, 19]. In the atomic limit ($W = 0$), the analogs of the lower and upper Hubbard subbands correspond to the energies $\Omega_v = E_0(d^n) - E_0(d^{n-1})$ and $\Omega_c = E_0(d^{n+1}) - E_0(d^n)$, respectively, where $E_0(d^n)$ is the energy of the ground term d^n of the configuration. It is assumed that the average number of electrons is $\langle n_d \rangle = n$. Then, the gap between the upper and lower Hubbard subbands is determined by the effective Hubbard parameter [18]

$$U_{\text{eff}}(d^n) = E_0(d^{n+1}) + E_0(d^{n-1}) - 2E_0(d^n). \quad (1)$$

Owing to the competition between the intra-atomic Hund’s exchange coupling J and the cubic component of the crystal field $10Dq$, each d^n term ($n = 4$ – 7) can have either HS or LS ground state [20, 21]. The HS–LS spin crossover can be due to a pressure-induced increase in the crystal field, which can also be approximated by the linear dependence $10Dq(P) = 10Dq(0) + \alpha_\Delta P$ [22]. As a result, spin crossover changes $U_{\text{eff}}(d^n)$, suggesting a relationship to the Mott–Hubbard transition. The effect of spin crossover on the electron correlation parameter turns out to be not universal: U_{eff} for d^5 ions is suppressed, whereas spin crossover increases U_{eff} for d^6 ions [12, 15, 22, 23].

3. In the case of CoO with the Co^{+2} ion having the d^7 configuration, the following two terms compete with each other with increasing pressure:

(i) the high-spin (HS) term with the spin $S = 3/2$ and the energy

$$E_{\text{HS}}(d^7) = E_C(d^7) - 8Dq - 11J; \quad (2)$$

(ii) the low-spin (LS) term with the spin $S = 1/2$ and the energy

$$E_{\text{LS}}(d^7) = E_C(d^7) - 18Dq - 9J. \quad (3)$$

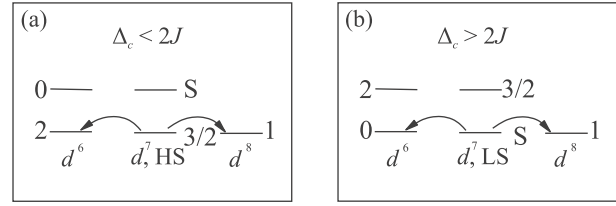


Fig. 1. Scheme of the multielectron terms corresponding to the neutral d^7 , hole d^6 , and electron d^8 configurations for (a) the high-spin ground state, when the crystal field is lower than the critical one $2J$, and (b) the low-spin state, when the crystal field is higher than the critical one $2J$. The numbers at the terms denote the values of spin. The arrows indicate the processes leading to the creation of a hole and an electron in the ground states.

Here, $E_C(d^7)$ is the spin-independent part of the Coulomb interaction for seven electrons at a Co^{2+} ion. According to these formulas, the high-spin state for a free ion at zero crystal field is more favorable in energy, but with an increase in the crystal field, the energy of the low-spin state decreases faster, and both energies become equal at $10Dq = 2J$. This condition corresponds to the pressure

$$P_S = (2J - 10Dq(0))/\alpha_\Delta. \quad (4)$$

To calculate the pressure dependence of effective Hubbard parameter (1), it is necessary to write the energies of the high- and low-spin terms of the configurations d^6 with one hole and d^8 with an additional electron in the form similar to Eqs. (2) and (3) (Fig. 1).

The corresponding expressions are presented in [15]. As a result, for both HS and LS states, we have

$$U_{\text{eff}}(d^7) = U - J, \quad (5)$$

which is independent of pressure. Thus, the Coulomb part of the band gap in CoO is independent of pressure, in contrast to oxides with d^5 and d^6 ions. The half-width of the band is $W = zt$, where z is the number of nearest neighbors and t is the hopping integral between the nearest neighbors, and does not depend on the spin state; therefore, spin crossover and the insulator–metal transition in CoO are independent.

4. To analyze the pressure dependence of the electrical resistance, it is necessary to take into account the dependence of the bandwidth on the interatomic distance, which leads to the following formula for the band gap:

$$E_g(P) = U - J - W(0) - \alpha_W P. \quad (6)$$

The structural transition from the cubic Cube I phase to the orthorhombic Rhom I phase at $P_{c1} = 43$ GPa can change the bandwidth by δW owing to the orthorhombic distortion. As a result, above the transition point in the Rhom I phase, the band gap can be represented as $E_g(P) = U - W(0) - \alpha_W P - \delta W$. In [14], there is no information on the presence of impurities and on

the mechanism of conductivity; therefore, we assume that the conductivity is of the activation type with the activation energy $E_a = E_g/2$. Then, from the magnitude of the stepwise change in the resistance by eight orders of magnitude at $P_{c1} = 43$ GPa at room temperature, we can estimate the jump in the band gap, $\delta W \approx 0.5$ eV. The other parameters in (6) at zero pressure ($U_{\text{eff}} = U - J$ and $W(0) = 6t_0$) are estimated using the Néel temperature $T_N = 290$ K [24] and the results of calculations of the parameters within the density functional theory (DFT) [25]. Using the constrained DFT method, the authors of [25] obtained $U = 5.1$ eV and $J = 0.9$ eV for CoO. Calculations of the band gap E_g in [25] carried out in various approximations give the following values for CoO: 2.21 eV (local-density approximation (LDA) + U), 2.47 eV (LDA + U + correlation corrections in the non-self-consistent G_0W_0 method), and 2.54 eV (LDA + U + correlation corrections in the partially self-consistent method GW_0). The measured values of the band gap for CoO are 2.5 ± 0.3 eV (obtained by photoelectron spectroscopy) [26, 27], 2.6 eV (by X-ray spectroscopy, XAS and XES) [28], and 2.5 eV (from optical absorption spectra) [29]. Therefore, in the further calculations, we use the zero-pressure band gap $E_g(0) = 2.5$ eV.

To estimate the interatomic hopping integral t_0 at zero applied pressure, we use the expression for the effective interatomic Heisenberg exchange interaction I_H according to the Kramers–Anderson superexchange mechanism in the Hubbard model,

$$I_H = 2t_0^2/U_{\text{eff}} = 2t_0^2/(U - J). \quad (7)$$

We estimate the I_H value using the mean-field Néel temperature

$$T_N = \frac{1}{3} I_H z S(S + 1) = 7.5 I_H. \quad (8)$$

Using the experimentally determined band gap (2.5 eV) and $T_N = 290$ K, as well as Eqs. (6)–(8), we find $t_0 = 0.076$ eV and $U - J = 3$ eV. For the Hund's exchange integral $J = 1$ eV (close to 0.9 eV from [25]), we obtain the Hubbard parameter $U = 4$ eV, which is in good agreement with the values reported in [25]. Note that the electron hopping parameter $t_0 = 0.076$ eV was obtained earlier for FeBO_3 [28], and this coincidence is not surprising because the metal–oxygen distance in octahedra is close to each other and the chemical bond is of the same type.

Using a Hund's exchange integral of 1 eV and the crystal field $10Dq(0) = 0.7$ eV [27] and assuming that the pressure derivative α_Δ for CoO is close to the corresponding parameter for FeBO_3 , $\alpha_\Delta = 0.018$ eV/GPa, we estimate the spin crossover pressure as $P_s = 72$ GPa, which is close to the values corresponding to the spin collapse calculated in [7]. The difference in ionic radii for the high-spin and low-spin states by about 10% usually leads to an isostructural transition character-

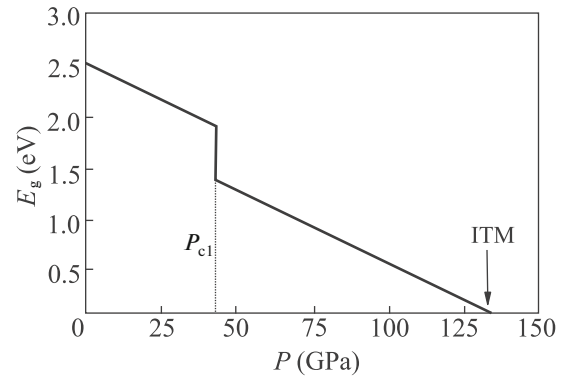


Fig. 2. Schematic pressure dependence of the electrical resistance for CoO exhibiting the stepwise change at the structural transition point P_{c1} and the insulator–metal transition (IMT).

ized by a pronounced volume change. The situation for CoO is more complicated owing to the existence of several structural phase transitions; therefore, the transition in the range of 80–90 GPa, which was attributed by the authors of [14] to spin crossover, is accompanied by a rather small (2.7%) volume change. Taking into account the stepwise change in the band gap at $P_{c1} = 43$ GPa, the expression valid in the entire pressure range can be written in the form

$$E_g(P) = \begin{cases} E_g(0) - \alpha_w P, & P < P_{c1}, \\ E_g(0) - \delta W - \alpha_w P, & P > P_{c1}. \end{cases} \quad (9)$$

The pressure derivative of the gap α_w , which is the only unknown parameter in Eq. (9), is estimated from the condition $E_g(133 \text{ GPa}) = 0$ as $\alpha_w = 0.015$ eV/GPa. The resulting pressure dependence of the electrical resistance is illustrated in Fig. 2 and qualitatively coincides with the experimentally determined curve reported in [14]. Near the insulator–metal transition point, the behavior of the system can be more complicated [30], but we consider only the qualitative picture in this work.

5. Let us discuss the change in the effective Heisenberg exchange coupling I_H in the case of spin crossover. In the conventional theory of the superexchange interaction of magnetic cations in the ground state via an intermediate anion, the antiferromagnetic exchange parameter is $I_H \sim t^2/U$ [31], where the parameter t describes the amplitude of the production of electron–hole pairs in the course of interband cation–anion–cation electron hopping and U is the band gap. Crossover-induced change in the ground state of a magnetic cation in the neutral configuration (Fig. 1), as well as possible crossovers in hole and electron configurations shown in Fig. 1, can change the type of overlap of the wavefunctions and thereby affect not only the magnitude but also the sign of the superexchange interaction. Earlier, it was shown that spin

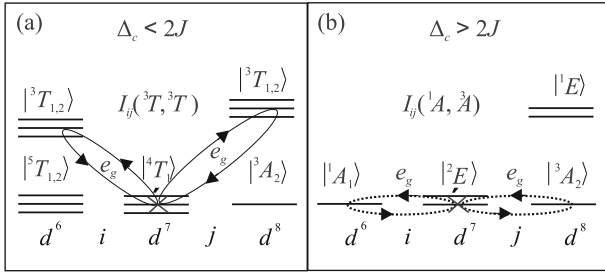


Fig. 3. Graphical diagram illustrating the formation of a virtual electron–hole pair providing the main contribution to the superexchange interaction between the i th and j th ions (a) in HS CoO at ambient pressure, where the AFM character of this interaction is due to the $I_{ij}(^3T^3T)$ contribution involving excited $^3T_{1,2}$ states and the σ -type overlap, and (b) in LS CoO at high pressure, where the FM character of this interaction is due to the contribution of $I_{ij}(^1A, ^3A)$ with the σ -type overlap.

crossover for FeBO₃ changes the sign of superexchange from antiferromagnetic in the HS state to ferromagnetic in the LS state [32]. The general theory of the superexchange interaction for various spin states of magnetic cations in d^2 – d^9 configurations was developed in [29], where a simple criterion was obtained for determining the nature (FM or AFM) of the superexchange interaction in transition metal oxides. Below, we apply the method developed in [33] to analyze the effect of spin crossover in CoO on the exchange coupling. The sign of the interaction is determined by the ratio of electron and hole spins, $S_\tau(d^8)$ and $S_\nu(d^8)$, respectively, at a virtual electron–hole pair in the $|\tau\rangle|\nu\rangle$ state, generated in the process of electron hopping from the i th to j th magnetic ion (see Figs. 3a and 3b). If $S_\tau(d^8) = S_\nu(d^6)$, the contribution to I_H from such a pair has an AFM character. If $S_\tau(d^8) = S_\nu(d^6) \pm 1$, this contribution is ferromagnetic. In the case of competition between them, the contribution with the largest σ -type orbital overlap prevails. According to this criterion, cobalt oxide at ambient pressure is an AFM material with the superexchange interaction

$$I_H = \sum_{i \neq j} I_{ij}(^3T, ^3T) \left(\hat{S}_i \hat{S}_j - \frac{1}{4} \hat{n}_i^{(e)} \hat{n}_j^{(h)} \right), \quad (10)$$

where $I_{ij}(^3T, ^3T)$ is the contribution from virtual hoppings of e_g electrons involving the $^3T_{1,2}$ states and corresponding to the σ -type overlap (Fig. 3a).

After spin crossover in the ground neutral $(3d^7)|4T_1\rangle \leftrightarrow |^2E\rangle$ and hole $(3d^6)|^5T_2\rangle \leftrightarrow |^1A_1\rangle$ states, the scheme of the superexchange interaction in CoO at high pressure changes. The spin in the ground term of the d^6 hole configuration is zero, whereas the spin for the electron d^8 configuration equals unity. As a result,

according to [33], the FM character of the interaction takes place in the LS state

$$I_H = - \sum_{i \neq j} I_{ij}(^1A, ^3A) \left(\hat{S}_i \hat{S}_j + \frac{1}{4} \hat{n}_i^{(e)} \hat{n}_j^{(h)} \right), \quad (11)$$

which is related to the $I_{ij}(^1A, ^3A)$ contribution and to the σ -type overlap, where $I_{ij}(^1A, ^3A)$ is the FM contribution from virtual hoppings of e_g electrons involving the ground 1A_1 and 3A_2 states and σ -type overlap (Fig. 3b). Thus, spin crossover at high pressure in CoO can lead to a change from the AFM to FM type of the magnetic ordering.

6. In conclusion, we emphasize that the pressure dependence of the electronic and magnetic properties of CoO, in comparison with other transition metal oxides, has both common features (metallization with increasing pressure and transition from the high-spin state to low-spin state) and clear differences. First, there is a slight correlation between spin crossover and the insulator–metal transition. For iron compounds with Fe³⁺ and Fe²⁺ ions having d^5 and d^6 configurations, respectively, crossover directly affects the Coulomb component of the band gap. We have shown that the Coulomb part of the gap for CoO does not change at the crossover point. In general, the volume change at the crossover point can change the bandwidth; this is a different mechanism of the spin crossover effect on the band gap.

Note that currently there is no direct experimental evidence of spin crossover in CoO. Spin crossover in iron compounds can be conveniently detected using the Mössbauer effect. However, this method is inapplicable for CoO. It is possible to observe spin crossover by detecting a pressure-induced change in the intensity of the low-energy satellite in high-resolution X-ray emission spectra, as was done in [34] for crossover in the paramagnetic phase of GdFe₃(BO₃)₄, but this is a rather nontrivial experiment. An indirect method for confirming spin crossover in CoO can involve revealing the transition between antiferromagnetic and ferromagnetic phases predicted in this work.

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