ISSN 1063-7761, Journal of Experimental and Theoretical Physics, 2015, Vol. 120, No. 1, pp. 132–138. © Pleiades Publishing, Inc., 2015.
Original Russian Text © K.A. Lobach, S.G. Ovchinnikov, T.M. Ovchinnikova, 2015, published in Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2015, Vol. 147, No. 1, pp. 149–156.

ELECTRONIC PROPERTIES OF SOLID

# Specific Features of Insulator–Metal Transitions under High Pressure in Crystals with Spin Crossovers of 3*d* Ions in Tetrahedral Environment

**K. A. Lobach[a]*, S. G. Ovchinnikov[a,b]**, and T. M. Ovchinnikova[c]**

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

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

[c] *Sukachev Institute of Forest, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

**e-mail: ks-ad@yandex.ru*

***e-mail: sgo@iph.krasn.ru*

Received July 12, 2013; in final form, July 8, 2014

**Abstract**—For Mott insulators with tetrahedral environment, the effective Hubbard parameter $U_{\text{eff}}$ is obtained as a function of pressure. This function is not universal. For crystals with $d^5$ configuration, the spin crossover suppresses electron correlations, while for $d^4$ configurations, the parameter $U_{\text{eff}}$ increases after a spin crossover. For $d^2$ and $d^7$ configurations, $U_{\text{eff}}$ increases with pressure in the high-spin (HS) state and is saturated after the spin crossover. Characteristic features of the insulator–metal transition are considered as pressure increases; it is shown that there may exist cascades of several transitions for various configurations.

**DOI:** 10.1134/S1063776115010045

## 1. INTRODUCTION

The experimental discovery of spin crossovers in a number of crystals with different structures has stimulated great interest in the study of various properties of such materials. As pressure increases, these materials exhibit variations in the magnetic, structural, and electronic properties. In a number of cases, the spin crossover induces an insulator–metal transition at high pressure. A detailed survey of a large number of experimental and theoretical studies on this subject was carried out by Lyubutin and Gavrilyuk [1].

Theoretical investigations of the effect of spin crossovers on an insulator–metal transition at high pressure in systems with octahedral symmetry of $d^n$ ions were carried out by Ovchinnikov [2, 3]. A large number of examples of Mott insulators with spin crossovers and insulator–metal transitions considered in the survey [1] refer to systems with $TO_6$ octahedra (here T is a 3*d* ion). At the same time, there are many crystals with tetrahedral symmetry of cations that contain $TO_4$ tetrahedra. In crystals with spinel or garnet structure, there are tetra- and octahedral sites simultaneously. There are crystals with only tetrahedral sites of 3*d* ions, for example, langasite $Ba_3TaFe_3Si_2O_{14}$ [4, 5]. This group of crystals also includes layered iron pnictides LaFeAsO with high-temperature superconductivity, as well as iron monosilicide FeSi. Thus, the analysis of the features of electron transitions in systems with tetrahedral symmetry of cations is of interest.

Since, in the standard Hubbard model [6], a transition from the insulator to metal state is possible under pressure, and a low-energy domain for the compounds of 3*d* metals can be described within a generalized Hubbard model, in the present paper we analyze in the spirit of this ideology the possibility of such transitions in crystals with tetrahedral symmetry.

A generalized Hubbard model [7] is constructed on the basis of local multielectron terms $d^{n-1}$, $d^n$, $d^{n+1}$, in a way similar to as the ordinary Hubbard model is formed on the basis of local terms $d^0$, $d^1$, and $d^2$. However, a significant difference between the generalized model and the standard model is that the spins of the terms $d^{n-1}$, $d^n$, $d^{n+1}$ can take different values $0 \le S \le 5/2$. In the generalized Hubbard model, the effective interaction parameter [8] is introduced, which is equal to

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

and determines the gap between an analog of the upper Hubbard band $\Omega_c = E_0(d^{n+1}) - E_0(d^n)$ and an analog of the lower Hubbard band $\Omega_v = E_0(d^n) - E_0(d^{n-1})$, where $E_0(d^n)$ is the energy of the ground term for a $d^n$ configuration.

For ions with $d^n$ configuration in the tetrahedral crystal field, there is a competition between different spin states, which is associated with the balance between the Hund exchange parameter $J$ and the splitting $\Delta = 10Dq$ due to the crystal field, This splitting depends on the interatomic distance and, hence, on pressure. Thus, an increase in pressure may induce

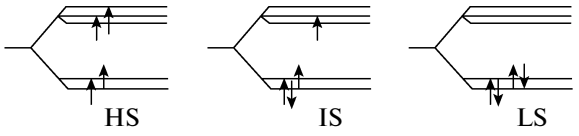


**Fig. 1.** Scheme of distribution of electrons for $d^4$ configuration in the HS, IS, and LS states.

spin crossovers, which, in turn, may lead to a variation in the effective interaction parameter $U_{\text{eff}}$. It turns out that, for systems with tetrahedral symmetry, the effective interaction parameter $U_{\text{eff}}$ is independent of pressure for configurations $d^1$, $d^3$, $d^6$, $d^8$, and $d^9$, decreases for $d^5$, and increases with pressure for configurations $d^2$, $d^4$, and $d^7$.

## 2. SPIN CROSSOVERS FOR $d^n$ CONFIGURATIONS

For ions of 3*d* metals in crystals with the dominant type of ionic bond, a characteristic situation is that of strong or intermediate crystal field [9]. In this case, the splitting of a one-electron atomic 3*d* level in the crystal field is taken into consideration first of all; then the split levels are filled, and multielectron terms are formed. Figure 1 demonstrates a scheme of electron distribution over orbitals for the $d^4$ configuration, which illustrates the calculations. We will assume that an $e_g$ electron has energy $-6Dq$ and a $t_{2g}$ electron has energy $+4Dq$. Without explicitly presenting the standard multiband Hamiltonian for a single unit cell (by which a $MeO_4$ cluster is meant), we notice the following intra-atomic Coulomb matrix elements: the intra-atomic Coulomb on a single orbital $U$, on different orbitals $V$, and the Hund exchange $J$; for spherically symmetric atoms, the relation $U = V + 2J$ holds. A pair of electrons on the same orbital with opposite spins has energy $U$, a pair of electrons on different orbitals with parallel spins has energy $V - J/2$, and a pair of electrons with opposite spins on different orbitals has energy $V$. Of course, the restriction of the analysis to such matrix elements is an approximation compared with the full multiplet theory [9–11], which is known as the Kanamori approximation [12]. This approximation correctly describes the ground term and a few excited terms; however, highly excited terms differ from the results of the full theory. When studying spin crossovers, we focus on the ground and the lowest excited terms, so that this approximation is adequate to the problem. It also preserves the symmetry properties of $d^n$ and $d^{10-n}$ terms.

This analysis makes clear that, for $d^2$, $d^7$, and $d^8$ configurations, the high-spin (HS) state is always implemented, irrespective of pressure and the values of the parameters $J$ and $\Delta$:

$$E_1^{(2)} = V - J/2 - 12Dq, \quad (2)$$

$$E_{3/2}^{(7)} = 21V - 3J/2 - 12Dq, \quad (3)$$

$$E_1^{(8)} = 28V - J/2 - 8Dq. \quad (4)$$

Here and below, $E_s^{(n)}$ is the energy of the $d^n$ configuration with spin $S$. For the $d^3$ configuration, two spin states are possible:

$$E_{3/2}^{(3)} = 3V - 3J/2 - 8Dq, \quad (5)$$

$$E_{1/2}^{(3)} = 3V + 3J/2 - 18Dq. \quad (6)$$

In this case, if the crystal field at zero pressure $\Delta_0$ ($\Delta = \Delta_0 + \alpha_d P$) is less than $3J$, the ground state in the range of pressures for $\Delta < 3J$ is the HS state ($S = 3/2$), whereas, for $\Delta > 3J$, the ground state is the low-spin (LS) state ($S = 1/2$). If $\Delta_0 > 2J$, then the ground state is always the LS state, and no spin crossover is observed.

For $d^4$ ions, there is a competition between three states (Fig. 1):

$$E_2^{(4)} = 6V - 3J - 4Dq, \quad (7)$$

$$E_1^{(4)} = 6V + 3J/2 - 14Dq, \quad (8)$$

$$E_0^{(4)} = 6V + 3J - 24Dq. \quad (9)$$

However, the state with intermediate spin (IS) is not implemented. A spin crossover (from $S = 2$ to $S = 0$) is observed for $\Delta = 3J$.

For $d^5$ ions, we have a similar situation: the system passes from the HS state to the LS state at $\Delta = 3.5J$:

$$E_{5/2}^{(5)} = 10\nu - 5J, \quad (10)$$

$$E_{1/2}^{(5)} = 10V + 2J - 20Dq. \quad (11)$$

The term $d^5$ with IS 3/2 has energy $E_{3/2} = 10V - J - 10Dq$ and is observed below the LS state in a free ion; however, it does not become the ground state at any pressure. Note also that a crossover from the HS to the LS state for $d^5$ ions in octahedral environment occurs for the same critical value $\Delta = 3.5J$.

The situation is changed for the $d^6$ configuration. Here the LS state with energy $E_0 = 15V + 3J - 16Dq$ is always above the IS state by $5J/2$; therefore, this state competes in energy with the highest ($S = 2$) and intermediate ($S = 1$) spins:

$$E_2^{(6)} = 15V - 3J - 6Dq, \quad (12)$$

$$E_1^{(6)} = 15V + J/2 - 16Dq. \quad (13)$$

A spin crossover occurs at $\Delta = 3.5J$.

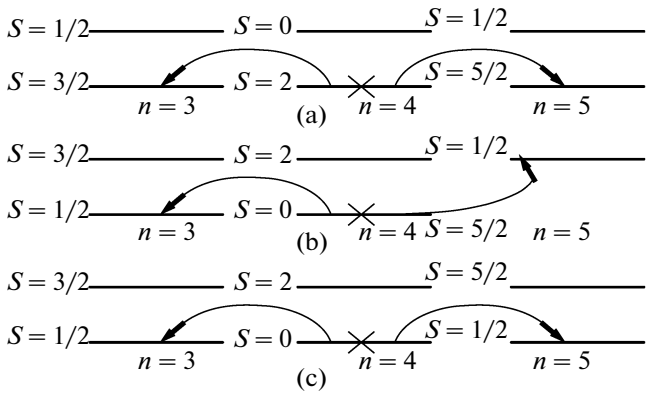


**Fig. 2.** Energy level diagrams that determine the effective interaction for $d^3$, $d^4$, and $d^5$ configurations for (a) $\Delta(P) < 3J$, (b) $3J < \Delta(P) < 3.5J$, and (c) $\Delta(P) > 3.5J$. The values of spins are indicated on the left of the levels. A state that is occupied at zero temperature is marked by a cross, and the arrows indicate possible processes of creation and annihilation of an electron.

## 3. PHASE TRANSITIONS FOR $d^4$ IONS

Let us determine the effective interaction parameter $U_{\text{eff}}$ as a function of pressure $P$ for this case. Its physical meaning is energy needed for an electron to jump from one atom to another:

$$U_{\text{eff}}(d^4) = E_0(d^5) + E_0(d^3) - 2E_0(d^4). \quad (14)$$

It is this parameter that defines the Mott–Hubbard gap

$$E_g = U_{\text{eff}} - W, \quad (15)$$

where $W$ is the half-width of the free electron band.

The effective interaction depends on the value of the crystal field $\Delta$, which, in turn, depends on pressure. Since the variations of the lattice parameter due to increasing pressure are relatively small, we will assume that the crystal field is a linear function of pressure:

$$\Delta = \Delta_0 + \alpha_d P. \quad (16)$$

As pressure increases, the half-width of the band $W = W_0 + \alpha_w P$ also increases. Finally, the gap between bands vanishes for a value of $W_c = aU_{\text{eff}}$, where $a \sim 1$. Therefore, the condition for the transitions of interest can be expressed as

$$W(P_t) = U_{\text{eff}}(P_t), \quad (17)$$

where $P_t$ is the phase transition point.

Thus, as pressure increases, each term ($d^3$, $d^4$, $d^5$) is characterized by a spin crossover from the HS to the LS state. For $d^3$ and $d^4$ configurations, the crossover occurs at $\Delta = 3J$, whereas, for $d^5$, at $\Delta = 3.5J$. Therefore, we can distinguish three domains in which these configurations have different diagrams of energy levels (Fig. 2).

(1) $\Delta(P) < 3J$. All terms are in the HS state, and the effective interaction is independent of the crystal field:

$$U_{\text{eff}}(P) = V - J/2. \quad (18)$$

(2) $3J < \Delta(P) < 3.5J$. For configurations $d^3$ and $d^4$, a transition to the LS state occurs, the ground state of the term $d^5$ is still the HS state, and the parameter $U_{\text{eff}}$ now depends on pressure:

$$U_{\text{eff}}(P) = U - 5J/2 + 10Dq. \quad (19)$$

(3) $\Delta(P) > 3.5J$. All terms are in the LS state, and the expression for the parameter $U_{\text{eff}}(P)$ coincides with (19), because nonzero matrix elements $\langle d^5, LS|d_6^+|d^4, LS\rangle$ relate the same states in Figs. 2b and 2c.

Thus, the effective interaction changes its behavior at the point $P_c = (3J - \Delta_0)/\alpha_d$ owing to the spin cross-

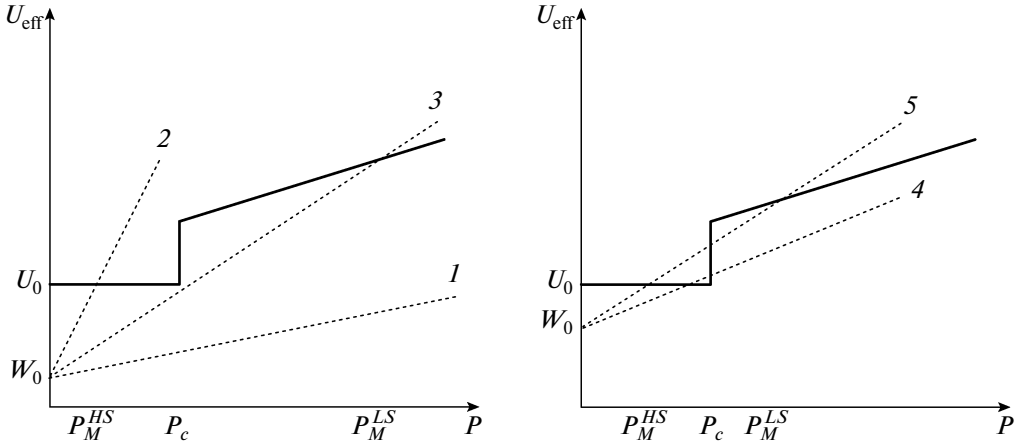


**Fig. 3.** Effective parameter $U_{\text{eff}}$ (solid line) and the half-width of the band $W$ (dotted lines) as a function of pressure for the $d^4$ configuration of a system whose ground state is insulator. The numbers indicate possible scenarios of behavior of such a system as pressure increases, depending on the parameters of the system: (*1*) insulator for any pressure, (*2*) insulator–metal transition in the HS state, (*3*) metal–insulator transition in the LS state, (*4*) successive insulator–metal–insulator transition, and (*5*) successive insulator–metal–insulator–metal transition.

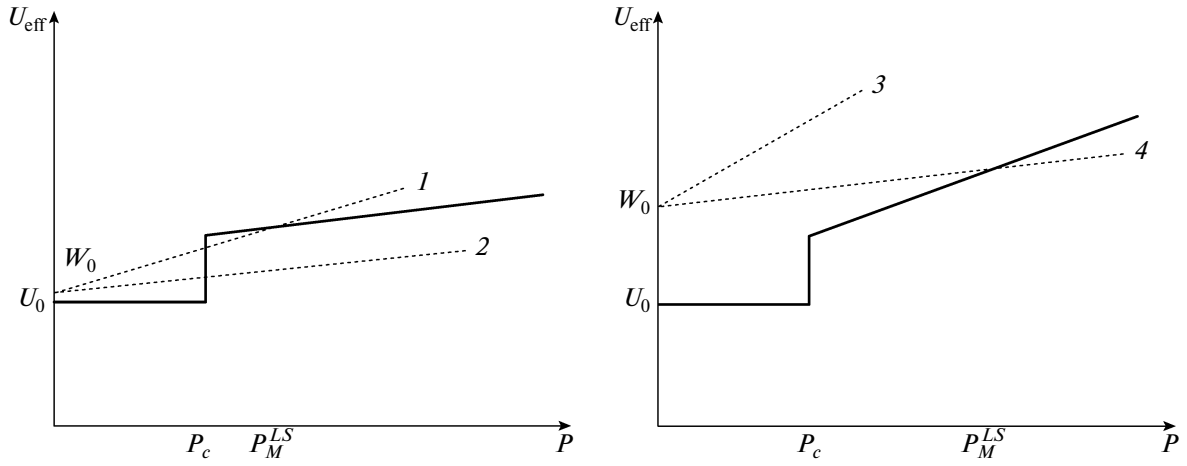


**Fig. 4.** Effective parameter $U_{\text{eff}}$ (solid line) and the half-width of the band $W$ (dotted lines) as a function of pressure for the $d^4$ configuration of the system whose ground state is metal. The numbers indicate possible scenarios of behavior of such a system as pressure increases, depending on the parameters of the system: (*1*) successive metal–insulator–metal transition, (*2*) metal–insulator transition at the spin crossover point, (*3*) metal for any pressure, and (*4*) metal–insulator transition in the LS state.

over, and the parameter $U_{\text{eff}}$ above this point increases with pressure.

Figure 3 demonstrates the effective interaction as a function of pressure and variants of behavior of the system whose ground state is insulator ($W_0 < U_0 = V - J/2$). There are five possible scenarios for such a system.

(1) Stable insulator. The system is always in the insulator state. This scenario is implemented under the following conditions:

$$\frac{\alpha_w}{\alpha_d} < \frac{V - J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w < \alpha_d. \tag{20}$$

(2) Insulator–metal transition. The system passes from the original insulator HS state to the metal HS state at the point

$$P_H^{MS} = \frac{V - J/2 - W_0}{\alpha_w}.$$

The mechanism of such a transition is completely determined by the growth of the half-width of the band $W$, as in the ordinary Hubbard model. The conditions for the implementation of this scenario are as follows:

$$\frac{\alpha_w}{\alpha_d} > \frac{V + J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w > \alpha_d. \tag{21}$$

(3) Insulator–metal transition in the range of LS states. In this case, the spin crossover notably increases the gap, as well as the pressure at which the insulator–metal transition occurs,

$$P_H^{LS} = \frac{V - J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}.$$

Such a situation occurs when

$$\frac{\alpha_w}{\alpha_d} < \frac{V - J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w > \alpha_d.$$

(4) Double insulator–metal–insulator transition. The first transition occurs in the HS state at the point $P_M^{HS}$, and then the system again passes to the insulator state at the spin crossover point $P_c$. Such a scenario is developed for $\alpha_w < \alpha_d$ and

$$\frac{V - J/2 - W_0}{3J - \Delta_0} < \frac{\alpha_w}{\alpha_d} < \frac{V + J/2 - W_0}{3J - \Delta_0}. \tag{22}$$

(5) Triple insulator–metal–insulator–metal transition. Due to the spin crossover, the system experiences a whole cascade of transitions. Again, successive transitions occur at the points $P_M^{HS}$ and $P_c$; then the system passes to the metal state in the range of pressures where all terms are already in the LS state. The transition point is

$$P_M^{LS} = \frac{V - 5J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}.$$

Necessary conditions for implementing such a scenario are the inequality $\alpha_w > \alpha_d$ and condition (22).

Figure 4 demonstrates variants of behavior of a system whose ground state is the metal state ($W_0 > U_0 = V - J/2$). Here also four variants of the effect of pressure on the system are possible. If the conditions (21) are satisfied, then the metal state is stable. If conditions (20) are satisfied, a transition to the insulator state at the spin crossover point occurs, whereas, if $\alpha_w < \alpha_d$ and conditions (22) are satisfied, then this transition occurs at the point $P_M^{LS}$. The last scenario is implemented for $\alpha_w > \alpha_d$ under conditions (22); successive transitions occur first to the insulator state at the point $P_c$, and then again to the metal state at the point $P_M^{LS}$.

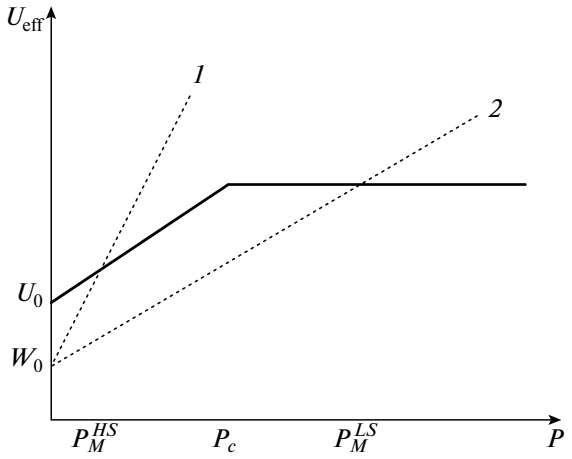


**Fig. 5.** Effective parameter $U_{\text{eff}}$ (solid line) and the half-width of the band $W$ (dotted lines) as a function of pressure for the $d^2$ and $d^7$ configurations of the system whose ground state is insulator. The numbers indicate possible scenarios of behavior of such a system as pressure increases, depending on the parameters of the system: (*1*) insulator–metal transition in the HS state and (*2*) insulator–metal transition in the LS state.

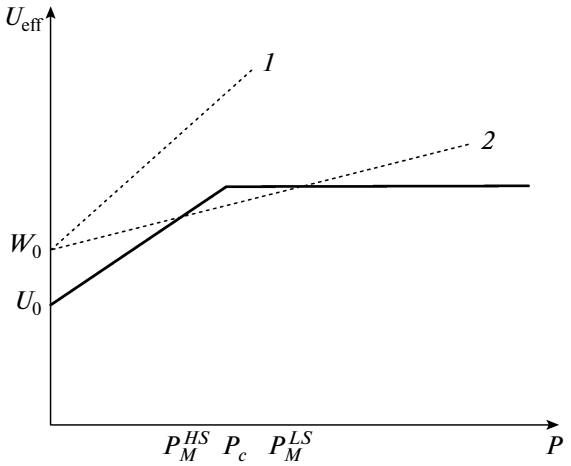


**Fig. 6.** Effective parameter $U_{\text{eff}}$ (solid line) and the half-width of the band $W$ (dotted lines) as a function of pressure for the $d^2$ and $d^7$ configurations of the system whose ground state is metal. The numbers indicate possible scenarios of the behavior of such a system as pressure increases, depending on the parameters of the system: (*1*) the system is in the metal state for any pressure and (*2*) successive metal–insulator–metal transition.

## 4. PHASE TRANSITIONS FOR $d^2$ AND $d^7$ IONS

In the case of $d^2$ and $d^7$ ions, the effective interaction parameter also increases with pressure. The analysis of the terms of $d^1$, $d^2$, and $d^3$ configurations and the spin crossovers in them yields two bands of pressures for $U_{\text{eff}}$:

$$U_{\text{eff}} = \begin{cases} V - J/2 + 10Dq, & P < P_c, \\ V + 5J/2, & P > P_c. \end{cases} \tag{23}$$

Here $P_c = (3J - \Delta_0)/\alpha_d$. For the case of $d^7$ ions, we have the following expression for the effective interaction:

$$U_{\text{eff}} = \begin{cases} V - J/2 + 10Dq, & P < P_c, \\ V + 3J, & P > P_c, \end{cases} \qquad P_c = \frac{3.5J - \Delta_0}{\alpha_d}. \tag{24}$$

The qualitative behavior of the parameter $U_{\text{eff}}$ and variants of behavior of the insulator (Fig. 5) and metal (Fig. 6) systems for increasing pressure are the same in these cases, while the conditions of phase transitions are different and are listed in the table. An interesting case is that where the system is metal from the very beginning. Then the spin crossover induces a successive metal–insulator–metal transition, which is essentially impossible for crystals without crossovers.

## 5. PHASE TRANSITIONS FOR $d^5$ IONS

For this configuration, the situation is distinctly different, and the correlation energy decreases as pressure increases (Fig. 7). The effective interaction parameter decreases by the following law as pressure increases:

$$U_{\text{eff}} = \begin{cases} V + 4J - 10Dq, & P < P_c, \\ V - J/2, & P > P_c, \end{cases} \qquad P_c = \frac{3.5J - \Delta_0}{\alpha_d}. \tag{25}$$

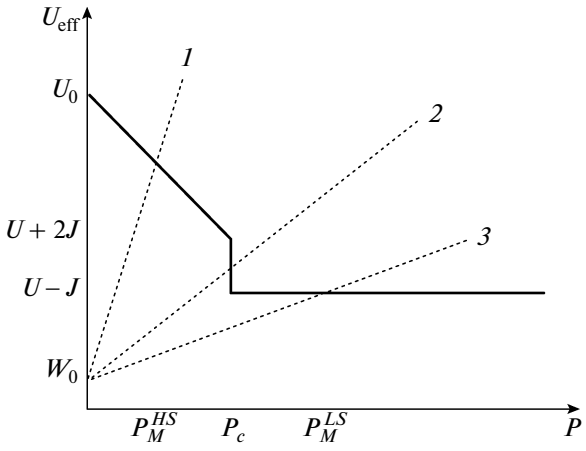


**Fig. 7.** Effective parameter $U_{\text{eff}}$ (solid line) and the half-width of the band $W$ (dotted lines) as a function of pressure for $d^5$ configurations of the system whose ground state is insulator. The numbers indicate possible scenarios of the behavior of such a system as pressure increases, depending on the parameters of the system: (*1*) transition to the metal state in the HS state, (*2*) transition to the metal state at the spin crossover point, and (*3*) transition to the metal state in the LS state.

Possible phase transitions and conditions for their implementation

| Type of behavior of the system | Conditions for $d^2$ ions | Conditions for $d^7$ ions |
|---|---|---|
| Insulator–metal (HS)<br>$W_0 < V - J/2 + \Delta_0$ | $\frac{\alpha_w}{\alpha_d} > \frac{V + 5J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w > \alpha_d$<br>Transition point<br>$P_M^{HS} = \frac{V - J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}$ | $\frac{\alpha_w}{\alpha_d} > \frac{V + 3J - W_0}{3.5J - \Delta_0}, \quad \alpha_w > \alpha_d$<br>Transition point<br>$P_M^{HS} = \frac{V - J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}$ |
| Insulator–metal (LS)<br>$W_0 < V - J/2 + \Delta_0$ | $\frac{\alpha_w}{\alpha_d} < \frac{V + 5J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w \le \alpha_d$<br>Transition point<br>$P_M^{LS} = \frac{V + 5J/2 - W_0}{\alpha_w}$ | $\frac{\alpha_w}{\alpha_d} < \frac{V + 3J - W_0}{3.5J - \Delta_0}, \quad \alpha_w \le \alpha_d$<br>Transition point<br>$P_M^{LS} = \frac{V + 3J - W_0}{\alpha_w}$ |
| Always metal<br>$W_0 > V - J/2 + \Delta_0$ | $\frac{\alpha_w}{\alpha_d} > \frac{V + 5J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w > \alpha_d$ | $\frac{\alpha_w}{\alpha_d} > \frac{V + 3J - W_0}{3.5J - \Delta_0}, \quad \alpha_w > \alpha_d$ |
| Metal–insulator–metal<br>$W_0 > V - J/2 + \Delta_0$ | $\frac{\alpha_w}{\alpha_d} < \frac{V + 5J/2 - W_0}{3J - \Delta_0}, \quad \alpha_w < \alpha_d$<br>Transition points<br>$P_M^{HS} = \frac{V - J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}$<br>$P_M^{LS} = \frac{V + 5J/2 - W_0}{\alpha_w}$ | $\frac{\alpha_w}{\alpha_d} < \frac{V + 3J - W_0}{3.5J - \Delta_0}, \quad \alpha_w < \alpha_d$<br>Transition points<br>$P_M^{HS} = \frac{V - J/2 + \Delta_0 - W_0}{\alpha_w - \alpha_d}$<br>$P_M^{LS} = \frac{V + 3J - W_0}{\alpha_w}$ |

The case when the system in the ground state is insulator is of interest. Then an insulator–metal transition always occurs. First, it can be implemented in the range of pressures where all terms are in the HS state. In this case, the main role is played by the strong dependence of the half-width of the band $W$ on pressure. The transition point is

$$P_M^{HS} = \frac{V + 4J - \Delta_0 - W_0}{\alpha_w - \alpha_d}.$$

If the dependence of the half-width of the band $W$ on pressure is weak, then the transition at the point

$$P_M^{LS} = \frac{V - J/2 - W_0}{\alpha_w}$$

is implemented precisely due to the spin crossover. The transition to the metal state can also occur at the spin crossover point

$$P_c = \frac{3.5J - \Delta_0}{\alpha_d}.$$

However, in the case of $d^5$ ions, the spin crossover opens new essential possibilities for the insulator–metal transition, in contrast to the case of $d^2$, $d^4$, and $d^7$ configurations. Such a transition would have anyway occurred under a pressure applied to the crystal. However, a quantitative effect for the critical pressure is quite significant. In cases (2) and (3), a transition to the metal state is achieved at much lower pressures compared with the value of $U_0/\alpha_w$ that would be needed for the transition to the metal state in the absence of the crossover.

## 6. DISCUSSION OF THE RESULTS

According to the results presented, spin crossovers under pressure significantly enrich the picture of insulator–metal transitions compared with the ordinary Hubbard model. It is important that this behavior is not universal and depends both on the ion configuration $d^n$ and on the symmetry of the local environment. The results obtained in the present study add to our understanding of earlier results [3] for octahedral environment. In either case, for systems with $d^5$ configurations, correlation phenomena are weakened as pressure increases; this fact facilitates the experimental observation of the insulator–metal transition. An example of such an effect of the spin crossover on the Mott–Hubbard transition for $BiFeO_3$ is described in [13]. The analysis of crossovers for the tetrahedral environment carried out in the present work, together with the previous analysis of the octahedral environment, has yielded identical critical values for $d^5$ ions; this fact sheds light on the crossover observed in yttrium iron garnet in the presence of iron ions both in the octa- and tetrahedral sites [1]. To demonstrate the

exact symmetry of terms in different sites, we present, for example, the energies of LS terms $d^4$ in a tetrahedral site ($6V + 3J - 24Dq$) and $d^6$ in an octahedral site ($15V + 3J + 24Dq$). Here the sign of $Dq$ is chosen to be positive for the tetrahedral site. The difference in the first summand is due to the Coulomb spin-independent contribution $Vn(n-1)/2$ [11].

For crystals with $d^2$, $d^4$, and $d^7$ ions in the tetrahedral environment, in addition to the effect of pressure on the ordinary mechanism of the Mott transition, we have predicted various exotic cases: cascades of several insulator–metal–insulator, insulator–metal–insulator–metal, as well as metal–insulator and metal–insulator–metal, transitions.

## ACKNOWLEDGMENTS

This work was supported by the program for supporting leading scientific schools (project no. NSh-2886.2014.2) and by the Presidium of the Russian Academy of Sciences within program no. 2.16.

## REFERENCES

1. I. S. Lyubutin and A. G. Gavrilyuk, Phys.—Usp. **52** (10), 989 (2009).
2. S. G. Ovchinnikov, J. Exp. Theor. Phys. **107** (1), 140 (2008).
3. S. G. Ovchinnikov, J. Exp. Theor. Phys. **116** (1), 123 (2013).
4. E. L. Belokoneva and N. V. Belov, Dokl. Akad. Nauk SSSR **260**, 1363 (1981).
5. B. V. Mill', E. L. Belokoneva, A. V. Butashin, G. G. Khodzhabagyan, and N. V. Belov, Dokl. Akad. Nauk SSSR **264**, 1385 (1982).
6. J. C. Hubbard, Proc. R. Soc. London, Ser. A **276**, 238 (1963).
7. V. V. Val'kov and S. G. Ovchinnikov, *Quasiparticles in Strongly Correlated Systems* (Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 2001) [in Russian].
8. J. Zaanen and G. A. Sawatzky, J. Solid State Chem. **88**, 8 (1990).
9. D. T. Sviridov and Yu. F. Smirnov, *The Theory of Optical Spectra of Transition-Metal Ions* (Nauka, Moscow, 1977) [in Russian].
10. G. Racah, Phys. Rev. **85**, 381 (1952).
11. Y. Tanabe and S. Sugano, J. Phys. Soc. Jpn. **9**, 753 (1954).
12. J. Kanamori, Progr. Theor. Phys. **30**, 275 (1963).
13. I. S. Lyubutin, S. G. Ovchinnikov, A. G. Gavriluk, and V. V. Struzhkin, Phys. Rev. B: Condens. Matter **79**, 085125 (2009).

*Translated by I. Nikitin*