The average value of the spin squared operator as an order parameter for spin phase transitions without spontaneous lowering of symmetry

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Abstract
Phase transitions from the low-spin to the high-spin state are a unique physical phenomenon without lowering of symmetry. In contrast to magnetic phase transitions, for which vector or tensor of physical quantities are used as order parameters, we have shown that for spin phase transitions the order parameter is a scalar quantity—the thermodynamic mean of spin square operator, which was not previously used at all in the theory of phase transitions. The free energy in the form of a functional of this order parameter is determined, and the phase diagrams for spin transitions are constructed. The influence of the pressure on spin transition is analyzed also. It is shown that the spin Hamiltonian with this order parameter allows one to obtain all possible spin transformations in compounds. At the same time, this order parameter correctly reflects the physical nature of the spin transition phenomena.

1. Introduction

For a multi-electron atom, the exchange interaction in accordance to the Hund rules leads to the ground state with the highest multiplicity [1, 2]. In solids, the ligand field should be taken into account, due to the action of which the low spin state can become the ground state of the ion [3]. In some solids, when the temperature changes, jump-like transitions are observed from the low spin (LS) state to the high spin (HS) state and vice versa [4–6]. A salutary change in the spin state can occur as a result of a structural phase transition (SPT) [7]. However, of particular interest is the abrupt change in the spin state of ions, which occurs without changing the structure and its symmetry [4, 5, 8]. In this case, they say that there is a spin phase transition (ST) between the spin states of a solid. ST can occur under the influence of changes in temperature [4, 9, 10], pressure [11–13], magnetic field [14], voltage [15, 16] and when exposed by light [17–21].

At present, when describing ST, it is customary to use the probability of populating of the high-spin state of the ion as the order parameter (OP) [4, 22] and, or the pseudospin \( \sigma = (N_{\text{HS}} - N_{\text{LS}})/(N_{\text{HS}} + N_{\text{LS}}) \), where \( N_{\text{HS}} \) and \( N_{\text{LS}} \) are the number of ions in the HS and LS states, respectively [23, 24]. Such approximation made it possible to develop thermodynamic [12, 22, 25], Ising-like [23, 24, 26], microscopic [27–29], numerical calculated [30, 31] and Landau [32] models when describing ST. In the Ising-like models used to describe spin transitions, the pseudospin \(+1\) and \( -1 \) are assigned to the high-spin and low-spin states. We emphasize that this is not a real spin, but a fabricated one. The average of this pseudospin is a non-physical vector, which is not present at spin transitions and does not correspond to physical reality in any way.

Despite the success of the Ising-like models [23, 24, 26, 33–40], the main drawback of these approaches is that population is a thermodynamic parameter, which does not allow constructing a full-fledged model starting from the Hamiltonian as, for example, in ferro- or antiferromagnets [41], and of the second is the problem of...
determining the thermodynamic mean of the pseudospin. However, there is no need to introduce pseudospin if the ion has a spin, so the theory should be built using the true spin of the ions.

The second, no less paradoxical fact is the use of interionic interactions in the form of Ising Hamiltonians with operators of projections of pseudospin ions. The Ising Hamiltonian is invariant under a change in the signs of the spin projections; therefore, formally, the phase transition in the Ising system is always associated with a decrease in symmetry. These essentially thermodynamic models postulate an expression for the thermodynamic interaction energy, written through the pseudospin, and not through the ion state operators.

Our proposed scalar order parameter—the average of the spin squared operator—eliminates these shortcomings and leads to a physically based understanding of the spin phase transition. The high-spin state and low-spin state are characterized by different values of the spin squared operator - these are real, not invented, physical quantities that characterize the state of ions.

The feature of ST is the appearance (presence) in the Mössbauer spectrum of lines corresponding to the HS or LS states of ions [42], which are characterized by different spin values (quantum number $S$) in these states. Therefore, experimentally, the difference between the level populations can be found by comparing the intensities of the lines of the HS and LS states [42, 43]. In Ising-like models, the order parameter $\sigma$ for the spin transition is independent of $S$.

In this article, we describe the ST using the effective Hamiltonian written through the operators of the square of the ion spin. Such a spin Hamiltonian containing highly symmetric operators $S^2$ makes it possible to describe the self-consistent effect of the crystal field on ion multiplicity in ST [44]. This approach allows one to take into account the level population and the value of ion spin $S$. The average value in experiments can be directly obtained from the magnetic susceptibility data [11]. Thus, the use of this order parameter is consistent with Mössbauer spectroscopy and with magnetic measurements.

The main result of our article is the statement that the order parameter in spin transitions is the thermodynamic average of the spin squared operator. This corresponds to symmetry and this is a special and original physical result.

### 2. Effective spin Hamiltonian

For simplicity, we restrict ourselves to considering only the two lowest levels of the ion. Let us take one of the most common cases when, due to the field of ligands surrounding the ion, the ground state of ions is the LS state with $S_0 = 0$, and in the nearest excited state $S_1 > 0$ figure 1(a). The distance between the levels is denoted $\Delta \varepsilon > 0$. This model corresponds to the effective spin Hamiltonian, which can be written as

$$\hat{H}_0 = \Delta \varepsilon \frac{\hat{S}^2}{S(S+1)}.$$  \hspace{1cm} (1)

For Hamiltonian (1) $\Delta \varepsilon > 0$, the ground state is the LS state, and the excited state is the HS state.

For a crystal consisting of ions whose states are described by the Hamiltonian (1), the OP is defined as the thermodynamic average:

$$\eta = \langle \hat{S}^2 \rangle = \frac{1}{N} \sum_n S_n (S_n + 1) = \sum_i p_i S_i (S_i + 1),$$  \hspace{1cm} (2)

where $N$ is the number of atoms in the crystal, $S_n$ is the spin of the ion whose position defines the vector $n$, $p_i$ are the probabilities of ionic states, $i = 0, 1$, for which $S_0 = 0, S_1 \neq 0$.

Note that the effective spin $\mu_{\sigma}^2$, measured in experiments with spin phase transitions, is proportional to the square root of the OP (2), $\mu_{\sigma}^2 = \mu_{\eta}^2 \eta$. In the experiment, one of the signs of the first order ST is a jump in the product of the magnetic susceptibility by the temperature, which is proportional to the square of the effective spin.

Being single-particle in nature, Hamiltonian (1) cannot lead to a cooperative effect. The possibility of critical behavior with ST can be obtained using the effective single-particle mean-field Hamiltonian

$$\hat{H}_f = \frac{\Delta \varepsilon}{S(S+1)} \hat{S}^2 - 2 J \eta \hat{S}^2,$$  \hspace{1cm} (3)

where $J$ is a constant that takes into account the coordination between the ligand field and ions.

Hamiltonian (3) contains a term proportional to the OP. The action of the second term in (3) can be associated with a change (decrease) in the size of the crystalline field during ST from the LS to the HS due to the effect of the coordinated action of the complexes on the crystal ions, figure 1(b).
Hamiltonian (3) differs from the Hamiltonian of the mean field of Ising-like models: (3) contains the operator of the square of the spin of the ion, and not the operator of the z-projection of the pseudospin in the first order.

The interaction energy of the system with the Hamiltonian (3), recorded per ion, is

$$E = \frac{\Delta \varepsilon}{S_i(S_i + 1)} \eta - J \eta^2.$$  

(4)

Note that one can arrive at energy (4) by writing the Hamiltonian with linear and bilinear terms in the operators of the square of the ion spins

$$\hat{H} = \frac{\Delta \varepsilon}{S_i(S_i + 1)} \sum_n S_n^2 - \sum_{nm} J_{nm} S_n^z S_m^z,$$  

(5)

where $J_{nm}$ is the constant of effective interaction between the $n$-th and $m$-th neighboring ions. In the mean field approximation, for the interaction of only the nearest neighbors, the equality $J = z J_{nm}$ is hold, where $z$ is the number of nearest neighbors. In Hamiltonian (5), the interionic interactions are written using the square of the spin operator, and not the first power of the pseudospin z-projection operator.

The approximation (5) suggests the possible interionic interactions, which are effectively described through the operators of the square of the ion spin. As in the case of Ising-like models, the second term in (5) is written phenomenologically, but unlike these models, it satisfies and corresponds to the symmetry of the ionic states of crystals with ST. Therefore, the Hamiltonian (5) is more preferred over Ising-like models. It should be emphasized that Hamiltonian (3) is more general, and Hamiltonian (5) is one of the possible cases. An interesting case is when the effective matching in (3) or the pairwise interactions in (5) lower the energy, that is, when the second term in (3) and (4) is minus and $J > 0$. The energy-lowering nonlinearity from the interaction contributes to the transition to the HS state.

Let us analyze the energy of the crystal (5) and the spectrum of the single-particle mean-field Hamiltonian (6) at $T = 0$ in the LS state, when the OP is equal to $\eta_0 = \eta(T = 0) = S_0(S_0 + 1) = 0$. The energy of the crystal at $T = 0$ in the LS state, $\eta_0 = 0$, is

$$E_0 = 0.$$  

(6)
The eigenvalues of the ion energy in the LS state are equal:

$$\varepsilon_{00} = 0, \quad \varepsilon_{01} = \Delta E.$$  (7)

Since at $T = 0$ and at $\Delta E > 0$ the lower singlet of the ion has a smaller energy $\varepsilon_{00} < \varepsilon_{01}$, the LS state is stable. If the OP at $T = 0$ is equal to $\eta = \eta(T = 0) = S_1(S_1 + 1)$, the energy (4) of the crystal in the HS state is

$$E_1 = \Delta \varepsilon - J S_1^2(S_1 + 1)^2.$$  (8)

The spectrum of the single-particle mean-field Hamiltonian (3) in the HS state has the form

$$\varepsilon_{00} = 0, \quad \varepsilon_{11} = \Delta \varepsilon - 2J S_1^2(S_1 + 1)^2.$$  (9)

From spectrum (9) we have that at $T = 0$ the HS state is stable if $\varepsilon_{10} > \varepsilon_{11}$ i.e., under the condition

$$\Delta \varepsilon < 2J S_1^2(S_1 + 1)^2 \text{ or } J > J_1 = \Delta \varepsilon / 2S_1^2(S_1 + 1)^2.$$  (10)

As a result, comparing (6) and (8), we find that at $T = 0$ the LS state will be in equilibrium if $E_0 < E_1$, i.e. at

$$\Delta \varepsilon > J S_1^2(S_1 + 1)^2 \text{ or } J < J_2 = \Delta \varepsilon / S_1^2(S_1 + 1)^2.$$  (11)

Thus, at $T = 0$ and for $J < J_1$, only the LS state will be stable and equilibrium. At $J_1 < J < J_2$ and $T = 0$, the LS state will be equilibrium, and the HS state will be stable, but nonequilibrium its energy is higher than the energy of the LS state. At $J > J_2$ the LS state will be stable at $T = 0$, but it will be nonequilibrium, and the HS state will be stable and equilibrium.

3. Free energy and equation of state

We use the standard definition of free energy $F = E - T\sigma$, where $\sigma$ is entropy. The entropy expression was derived using its standard definition: $\sigma = -\sum_k p_k \ln p_k$, where $p_k$ are probabilities. Only the spin degrees of freedom were taken into account, the degeneracy multiplicity of the second level is equal $2S_1 + 1$. Based on one ion, free energy is written as

$$F(\eta) = \Delta \varepsilon \frac{\eta}{S_1(S_1 + 1)} - J\eta^2 + T \left( \frac{\eta}{S_1(S_1 + 1)} \ln \frac{\eta}{S_1(S_1 + 1)(2S_1 + 1)} \right) + \left( 1 - \frac{\eta}{S_1(S_1 + 1)} \right) \ln \left( 1 - \frac{\eta}{S_1(S_1 + 1)} \right).$$  (12)

we find the equation of state from the condition $dF(\eta)/d\eta = 0$ in the form

$$\frac{\Delta \varepsilon}{S_1(S_1 + 1)} = 2J\eta - \frac{T}{S_1(S_1 + 1)} \ln \left( \frac{(2S_1 + 1)(S_1(S_1 + 1) - \eta)}{\eta} \right) = 0.$$  (13)

For the convenience of calculations and a graphical representation of the results, we normalize the energy and the parameters included in it by $\Delta \varepsilon/S_1(S_1 + 1)$ and introduce the designations:

$$f = \frac{F}{\Delta \varepsilon/S_1(S_1 + 1)}, \quad \eta = \frac{J}{\Delta \varepsilon/S_1(S_1 + 1)}, \quad t = \frac{T}{\Delta \varepsilon/S_1(S_1 + 1)}.$$  (14)

Depending on the magnitude of the interaction parameter, equation of state (13) gives three types of solutions. Further, for an example, we give the solutions calculated for $S_1 = 2$.

3.1. Continuous solutions

In figure 2 the solutions of equation (13) for the interaction parameter $j = 0$, $=0.067$, $=0.083$ are shown. The OP value changes continuously from temperature. At $t \to \infty$, the equilibrium value of OP is $\eta(t \to \infty) = \eta_{t \to \infty} = 5$.

The derivative of the order parameter with respect to temperature is higher of zero (see the inset in figure 2). The temperature dependence of $d\eta/dt$ has a maximum. The value of the derivative at the maximum point increases with an increase in the interaction parameter $j$. The area of existence of continuous solutions is $j < 0.09245$.

3.2. S-type solutions

Such solutions can be obtained from equation (13), provided that the interaction parameter takes a value from the interval $0.09245 < j < 0.1$. In figure 3, for example, is shown the solution $\eta(t)$ of the equation of state for $j = 0.097$. The low-spin part of OP exists for $t < t_{LS}$ and its derivative $d\eta_{LS}(t)/dt > 0$. A high-spin branch of
the solution $\eta_{HS}(t)$ exists for $t > t_{HS}$ and for it $d\eta_{HS}(t)/dt > 0$ as well. The branch of the solution in the interval $t_{HS} < t < t_{LS}$ with $d\eta(t)/dt < 0$ is unstable (see the inset in figure 3).

At the point of ST $t_C$, the energy of the LS state is equal to the free energy of the HS state $f_{LS}(t_C) = f_{HS}(t_C)$ (see the inset in figure 3). The jump in the order parameter at $t_C$ in figure 3 is shown by vertical line with two oppositely directed arrows. The order parameter $\eta$ is a scalar, a change in its value does not lead to a change in symmetry, therefore this is an isostructural phase transition of the first order [32].

At nonequilibrium transition between LS and HS states, hysteresis is possible. Upon transition from the HS to the LS, its left boundary $t_{LS}$ is indicated by vertical dashed line with down arrows. Upon transition from LS to HS, the right hysteresis boundary is indicated by vertical line with up arrows. Hysteresis is limited by two points $t_{HS}$ and $t_{LS}$.

For temperatures $t < t_C$, the LS state with OP $\eta_{LS}(t)$ will be stable and equilibrium. For $t_C < t < t_{LS}$, the LS state with OP $\eta_{LS}(t)$ will be stable, but nonequilibrium (metastable state). The HS state with OP $\eta_{HS}(t)$ is stable and equilibrium for $t > t_C$. At $t_{HS} < t < t_C$ the HS state is stable, but nonequilibrium (metastable state).

Figure 2. Temperature dependences of the order parameter on the normalized temperature $t$. Curve 1 is plotted for $j = 0$, curve 2 is for $j = 0.067$, curve 3 is for $j = 0.083$. The inset shows the field dependences for the derivatives of the OP with respect to temperature.

Figure 3. The dependence of the order parameter on the normalized temperature $t$ for $j = 0.097$. The inset shows the free energy dependence $f(t)$ for this solution. $t_C$ is the temperature of the ST, $t_{LS}$ is the temperature of the LS state stability, $t_{HS}$ is the temperature of the HS state stability.

\[ f(t) = \frac{1}{2} \eta^2 \]
3.3. Bursting solutions and crossover

Such solutions can be obtained from equation (13) if the interaction parameter takes a value from the interval $0.1 < j < 0.166$. In figure 4 is shown the temperature dependence of $\eta(t)$, obtained from equation (13) for $j = 0.125$. The solution has two branches that do not continuously pass into each other.

A stable LS solution branch $\eta_{LS}(t)$ exists for $t < t_{LS}$ and its derivative $d\eta_{LS}(t)/dt > 0$ [11, 45]. The HS branch has a solution with OP $\eta_{HS}(t) \rightarrow \eta_{-\infty} = 5$ and this solution is stable for all temperatures $t > t_{HS} = 0$, and the equilibrium at $t > t_{C}$. For the HS solution, the derivative of OP with respect to temperature is negative. Despite the fact that $t_{HS} = 0$ is the boundary temperature of stability for the HS state, the temperature of the equilibrium ST between the LS and HS states is finite (see the inset in figure 4). For solution $\eta_{HS}(t)$, the ground state is the HS state of the ion, and the LS state is excited. Therefore, a crossover of ionic states occurs at the point of the ST.

4. Phase diagram

As can be seen from figures 3 and 4 theoretical temperatures $t_{C}$, $t_{LS}$, $t_{HS}$ depend on the interaction parameter $j$. These dependences are shown in the phase $j - t$ diagram in figure 5. In the tricritical point, the curves of three dependences converge. Coordinates of the tricritical point are: $j_{tr} = 0.09245$, $t_{tr} = 1.698$. For the first order ST, from LS to HS the condition $j > j_{tr}$ must be satisfied. For $j > 1$ at the point of phase transition a crossover of ionic states occurs.

At $j > 0.1$ the critical temperature of the loss of stability of the HS state is $T = 0$, $t_{HS}(j > 0.1) = 0$ that is, this state is stable in the entire temperature range, but only for $t > t_{C}$ it is equilibrium. Another feature of this model is the linear dependence of the critical temperature of the ST

$$t_{C}(j_{tr} \leq j \leq 1/6) = t_{tr}(1 - (j - j_{tr})/(1/6 - j_{tr})).$$

(15)

The model parameters $J$ and $\Delta \varepsilon$ can be renormalized by spin-elastic interactions and external pressure. Thus, the effect of elastic long-range action is taken into account.
5. ST induced by compression

During compression, in the interaction energy it is necessary to take into account the elastic contribution and the change in the values of the model parameters \( \Delta \varepsilon = \Delta \varepsilon(\gamma) \), and, \( J = J(\gamma) \) where \( \gamma = \Delta V/V \) is the relative change of volume under applied pressure \( p \).

In the linear approximation, the dependence of the model parameters on the relative change in volume can be represented as

\[
\Delta \varepsilon(\gamma) = \Delta \varepsilon(\gamma = 0) + (d\Delta \varepsilon(\gamma)/d\gamma)_{\gamma = 0} \gamma = \Delta \varepsilon_0 + \alpha_1 \gamma,
\]

\[
J(\gamma) = J(\gamma = 0) + (dJ(\gamma)/d\gamma)_{\gamma = 0} \gamma = J_0 + \alpha_2 \gamma,
\]

where \( \Delta \varepsilon_0 = \Delta \varepsilon(\gamma = 0) \), \( \alpha_1 = (d\Delta \varepsilon(\gamma)/d\gamma)_{\gamma = 0} \), \( J_0 = J(\gamma = 0) \), \( \alpha_2 = (dJ(\gamma)/d\gamma)_{\gamma = 0} \).

Substituting (16) and (17) into (4) and minimizing it together with the elastic contribution of energy, we find the dependence of the relative compression on OP

\[
\gamma = \frac{1}{k} \left( p - \frac{\alpha_1}{S_1(S_1 + 1)} \eta + \alpha_2 \eta^2 \right),
\]

where \( k \) is the elastic modulus.

If \( p = 0 \) the spontaneous deformation during ST depends only on the value of OP:

\[
\gamma(p = 0) = \frac{1}{k} \left( -\frac{\alpha_1}{S_1(S_1 + 1)} \eta + \alpha_2 \eta^2 \right).
\]

The onset of spontaneous deformation during the ST transition is a consequence of the effect of phonon excitations on the spin states of ions. In the point of the ST, the OP jump gives a jump in relative change of the volume:

\[
\Delta \gamma(p = 0) = \gamma_{HS}(p = 0) - \gamma_{LS}(p = 0) = \frac{\eta_{HS} - \eta_{LS}}{\kappa} \left( -\frac{\alpha_1}{S_1(S_1 + 1)} \right)
\]

\[
+ \alpha_2 (\eta_{HS} + \eta_{HTS}).
\]

Usually, in the case of ST from the LS to the HS state the \( \Delta \gamma(p = 0) > 0 \) in the transition point what is possible, for example, with \( \alpha_2 > 0 \) and \( \alpha_1 < 0 \).

The pressure \( p \) renormalizes the model parameters in (12) and additionally gives terms of the third and fourth degree of the OP in (4). In the linear approximation (19), (20), the action of these terms can be neglected. In this case, the interaction energy \( E(\eta, p) \) takes the form:
\[
E(\eta, p) = \frac{1}{2\kappa}p^2 + \left( \frac{\Delta \varepsilon_0}{S_1(S_1 + 1)} + \frac{1}{\kappa} \frac{\alpha_1 p}{S_1(S_1 + 1)} \right) \eta - \left( J_0 + \frac{1}{2\kappa} \frac{\alpha_1^2}{S_1^2(S_1 + 1)^2} \right) \eta^2.
\]

At \( p = 0 \), the contribution of spin-elastic interactions to the energy is negative and decreases the total energy. As can be seen from (21), external pressure renormalizes the coefficients in energy (4) and therefore it can affect the phase transition and the position of critical points [11, 29, 45].

ST is always accompanied by a change in volume. However, if \( \alpha_1 \) and \( \alpha_2 \) are of the same sign, then the contribution to the energy from spin-elastic interactions is small and spontaneous deformation has small effect on the ST. In this case it will not prevent the formation of an inhomogeneous (for example, two-phase) spin state [46].

Spin-elastic interactions renormalize the conditions for the occurrence of ST. It follows from (21) that for ST it is necessary that the model parameters satisfy the inequality

\[
J_0 + \frac{1}{2\kappa} \frac{\alpha_1^2}{S_1^2(S_1 + 1)^2} > 0.09245 \Delta \varepsilon_0 / S_1(S_1 + 1).
\]

So, at \( p = 0 \), the spin-elastic interaction effectively increases the interionic interactions, the coefficient of \( \eta^2 \) increases, and thus the spin-elastic interaction contributes to the ST.

Pressure can induce ST. If condition (22) is not satisfied for a free crystal, then there is no ST. However, for example, at \( \alpha_2 > 0 \) and \( \alpha_1 < 0 \) during compression, pressure induces an ST if it is greater than the critical pressure \( p > p_c \):

\[
p > p_c = \kappa \frac{0.09245 \Delta \varepsilon_0 - J_0 S_1(S_1 + 1) - \alpha_1^2 / 2\kappa S_1(S_1 + 1)}{\alpha_2 S_1(S_1 + 1) - 0.09245 \alpha_1}.
\]

The value of \( p_c \) is proportional to the modulus \( \kappa \); therefore, for elastically soft crystals, for appearance of ST, small compression is sufficient.

It is clear that the opposite process is possible when the ST exists at \( p = 0 \), and upon compression it ceases to exist. This is a consequence of the fact that upon compression of the sample, spin-elastic interactions shift the position of the tricritical point in the phase diagram, it can turn out to the right (pressure suppresses ST) or to the left (pressure induces ST). This model result substantiates the diversity of phase diagrams of ST obtained in the phenomenological theory [4, 5, 12, 16]. The result of the model, that pressure can induce or suppress ST, is in good agreement with experimental data on the observation of ST during compression of crystals [17, 47–50].

6. Conclusions

Thus, the theory of the ST has been developed, which is constructed using the thermodynamic average operator of the square of the spin as order parameter. This order parameter has not been discussed in the literature before, it is a scalar quantity, so when it changes, the symmetry does not change. This choice of OP is due to and corresponds to the type of magnetic transition, in which there is no change in symmetry and which is an isostructural phase transition between two states with different values of \( \langle S^2 \rangle \) and of magnetic susceptibility. This is what distinguishes a spin phase transition from a ferromagnetic phase transition, in which the order parameter is a vector, and the average from the spin square operator is preserved.

It is shown that spontaneous deformation of a free crystal promotes ST. Pressure affects the magnitude of the spin-elastic bond and it can induce or suppress ST.

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