

# Charge ordering in mixed-valence cluster systems

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Crystals containing mixed-valence exchange clusters as a structural unit are predicted to have a charge ordering. One or two phase transitions are shown to occur in such systems. The magnetic moment of a charge-ordered crystal is predicted to have an anomalous temperature dependence.

1. Semiclassical mixed-valence theory<sup>1-3</sup> was used to explain the ferromagnetism of several oxides in terms of delocalization (tunneling) of an extra electron inside a cluster of mixed-valence ions (double exchange). The results obtained in Refs. 1–3 refer essentially to the unit cell of the crystal, so that the problem involving the phase state of the crystal dropped out in those studies. In this letter we show that the conceptual understanding of the magnetism of mixed-valence systems changes qualitatively and quantitatively when the interaction between clusters and the Heisenberg exchange (which is disregarded in the semiclassical theory) are taken into account.

2. We will use the results of the quantum theory of mixed valence<sup>4</sup> for the transition ions, which take into account the exchange interaction, along with the crystal fields. We will use the model of a biocahedral cluster with a common axis<sup>4</sup>  $C_4(z)$ . The spectrum of the cluster consists of a series of Coulomb multiplets which are split by the exchange and tunnel interactions.<sup>4</sup> The energies of the steady states  ${}^4A_{1g,2u}$  and  ${}^2A_{1g,2u}$  are determined by the parameters of the Heisenberg exchange interaction  $J$  and the transfer  $P$ . We can write the Hamiltonian of the crystal as

$$H = \sum_n H_n - \sum_{n,m} K(n-m) d_n^z d_m^z, \quad (1)$$

$$H_n = \begin{pmatrix} {}^4A_{1g} & {}^4A_{2u} & {}^2A_{1g} & {}^2A_{2u} \\ 0 & 0 & 0 & 0 \\ 0 & 2P & 0 & 0 \\ 0 & 0 & \frac{3}{2}(J+P) & 0 \\ 0 & 0 & 0 & \frac{1}{2}(3J+P) \end{pmatrix}, \quad d_n^z = \begin{pmatrix} {}^4A_{1g} & {}^4A_{2u} & {}^2A_{1g} & {}^2A_{2u} \\ 0 & d_1 & 0 & 0 \\ d_1 & 0 & 0 & 0 \\ 0 & 0 & 0 & d_2 \\ 0 & 0 & d_2 & 0 \end{pmatrix} \quad (2)$$

$$K(\mathbf{n} - \mathbf{m}) = (3\cos^2\theta_{nm} - 1)R_{nm}^{-3},$$

$$d_1 = \langle {}^4A_{1g} | d^z | {}^4A_{2u} \rangle, \quad d_2 = \langle {}^2A_{1g} | d^z | {}^2A_{2u} \rangle. \quad (3)$$

$H_n$  is the Hamiltonian of an isolated cluster with the eigenvalues found in Ref. 4. The second term in (1) describes the dipole-dipole interaction of the clusters, and  $d_n^z$  is the dipole-moment matrix. Excluding from consideration the nonorthogonal nature of the atomic functions of the  $a$  and  $b$  ions of the cluster, we can write  $d_1 = d_2 = (eR/2) = d_0$ , where  $R = R_{ab}$ . In the molecular-field approximation, the eigenvalues  $\epsilon(S)$  of the cluster's Hamiltonian are

$$\epsilon_{1,2} = \left(\frac{3}{2}\right) = P \pm W_1, \quad \epsilon_{3,4} = \frac{3}{2}J + P \pm \frac{1}{2}W_2,$$

$$W_1 = (P^2 + L^2 d_0^2 \bar{d}^2)^{1/2}, \quad W_2 = (P^2 + 4L^2 d_0^2 \bar{d}^2)^{1/2}, \quad L = \sum_n K(\mathbf{n} - \mathbf{m}). \quad (4)$$

For the expectation value of the dipole moment,  $\bar{d}$ , which is the order parameter, we write the equation

$$\frac{1}{|L| d_0^2} = \frac{W_1^{-1} \sinh\left(\frac{W_1}{kT}\right) + W_2^{-1} \sinh\left(\frac{W_2}{2kT}\right) \exp\left(-\frac{3J}{2kT}\right)}{\cosh\left(\frac{W_1}{kT}\right) + \frac{1}{2} \cosh\left(\frac{W_2}{2kT}\right) \exp\left(-\frac{3J}{2kT}\right)}. \quad (5)$$

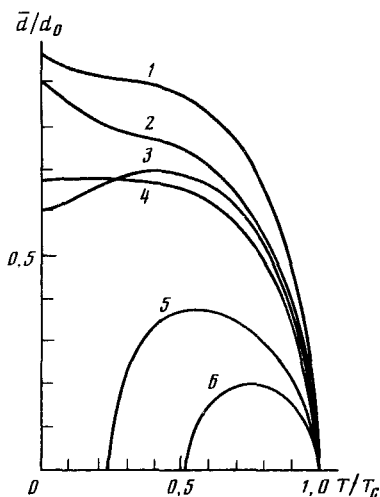


FIG. 1. Temperature dependence of the order parameter for  $J < 0$ . 1— $y = 0.5$ ,  $x = 0.3$ ; 2— $y = 0.8$ ,  $x = 0.3$ ; 3— $y = 0.8$ ,  $x = 0.05$ ; 4— $y = 0.9$ ,  $x = 0.25$ ; 5— $y = 1.1$ ,  $x = 0.2$ ; 6— $y = 1.1$ ,  $x = 0.1$ .

It is clear from physical considerations that the electron density distribution in the ground state of the crystal is determined by the competition between the double exchange, which causes the delocalization of the "extra" electron, and the dipole-dipole interaction of the clusters, which stabilizes the charge-ordered phase. The behavior of the system is determined by two dimensionless parameters  $x = |J|/|P|$  and  $y = |P|/|L|d_0^2$ . Analysis of Eq. (5) shows that a single phase transition occurs in the case of a Heisenberg antiferromagnetic exchange ( $J < 0$ ) for  $y \leq 1$  and arbitrary  $x$  or  $2 > y \gg 1$ ,  $x > 1/3$ . The low-temperature limit of  $\bar{d}$  is defined as  $\bar{d} = d_0(1 - y^2)^{1/2}$  for  $y \leq 1$ ,  $x < x_1$  or  $\bar{d} = d_0(1 - y^2/4)^{1/2}$  for  $y \leq 1$ ,  $x > x_2$  and  $2 > y \gg 1$ ,  $x > 1/3$ , where  $x_1 = \frac{2}{3}[(1/y^2 + \frac{3}{4})^{1/2} - 1/y]$  and  $x_2 = \frac{2}{3}[1/y - (1/y^2 - \frac{3}{4})^{1/2}]$  (curves 1-3 in Fig. 1). For  $y \leq 1$ ,  $x_1 < x < x_2$  the value of  $\bar{d}$  is determined numerically in the limit  $T \rightarrow 0$  (curve 4 in Fig. 1). For  $1 < y \leq 4/3$ ,  $x^*(y) < x \leq 1/3$  [where  $x^*(y)$  is determined numerically] the temperature dependence of the order parameter is nonmonotonic and the system may have two phase transitions at  $T'_c$  and  $T_c$ ; here the charge-ordered state occurs in the interval  $T'_c < T < T_c$  (curves 5 and 6 in Fig. 1). This result can be explained qualitatively in the following way. At low temperatures when the ground level  ${}^4A_{1g}$  ( $P > 0$ ) is filled, the electron cannot be localized in a system with a tunnel parameter  $2P$ , and the filling of the  ${}^2A_{2u}$  level moderates the conditions for the stabilization of the charge-ordered phase. A further increase of the temperature leads to the filling

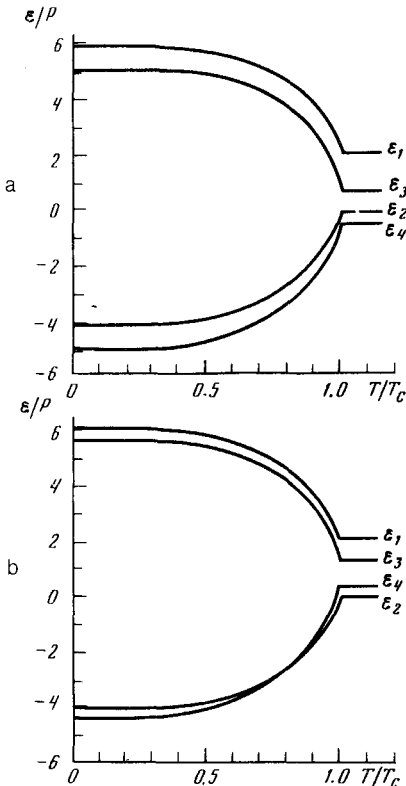


FIG. 2. Temperature dependence of the energy levels of a cluster in the mean-field approximation for  $J < 0$  and  $P > 0$ . (a)  $y = 0.2$ ,  $x = 0.6$ ; (b)  $y = 0.2$ ,  $x = 0.2$ .

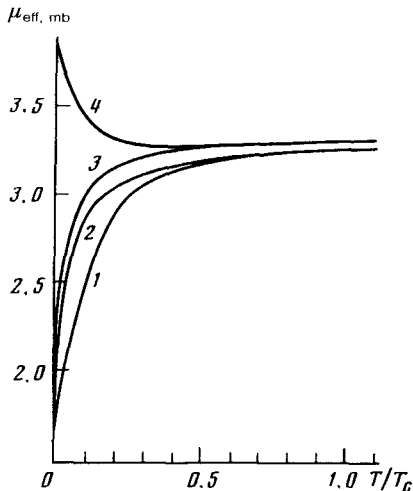


FIG. 3. Temperature dependence of the effective magnetic moment for  $J < 0$ . 1— $y = 0.2$ ,  $x = 0.6$ ; 2— $y \rightarrow \infty$ ,  $x = 0.6$ ; 3— $y = 0.2$ ,  $x = 0.2$ ; 4— $y \rightarrow \infty$ ,  $x = 0.2$ .

of the  ${}^2A_{1g}$  level and the system again undergoes a transition to the paraelectric state. In the case of a Heisenberg ferromagnetic exchange ( $J > 0$ ), the gap between the  ${}^2A_{2u}$  and  ${}^4A_{1g}$  states increases with increasing  $J$  and the conditions for the appearance of two phase transitions become more rigid. For  $y \leq 1$  and arbitrary values of  $x$  we have  $\bar{d}(T=0) = d_0(1-y^2)^{1/2}$ .

3. The temperature dependence of the mean field leads to a temperature-dependent level scheme (Fig. 2), which accounts for the nontrivial behavior of the magnetic moment (Fig. 3). In particular, the anomalous behavior of the magnetic moment (curve 3 in Fig. 3) stems from the fact that the change in the temperature when  $y < 1, \frac{2}{3} [1/y - (1/y^2 - \frac{3}{4})^{1/2}] < x < \frac{1}{3}$  leads to a crossing of the levels and to a transition between two paramagnetic states of the crystal with  $S = 1/2$  and  $S = 3/2$  (Fig. 2b). At low temperatures the mean electric field suppresses the ferromagnetism, so that the conclusions of Ref. 2 concerning the ferromagnetic ground state of the mixed-valence systems have certain restrictions. Apart from the double exchange, the Heisenberg exchange and the intercluster interaction figure prominently in the formation of the ground state. We wish to stress that the temperature-induced transition between two paramagnetic states of the crystal is associated with nonmagnetic interactions. The results obtained by us can be applied directly to the cluster systems<sup>5</sup> and can apparently describe semiquantitatively the properties of mixed-valence crystals.

<sup>1</sup>C. Zener, Phys. Rev. **82**, 403 (1951).

<sup>2</sup>P. W. Anderson and H. Hasegawa, Phys. Rev. **100**, 675 (1955).

<sup>3</sup>P. G. de Gennes, Phys. Rev. **118**, 141 (1960).

<sup>4</sup>M. I. Belinskii and B. S. Tsukerblat, Fiz. Tverd. Tela **26**, 758 (1984) [Sov. Phys. Solid State **26**, 458 (1984)].

<sup>5</sup>Mixed-Valence Compounds, ed. D. B. Brown, Oxford: D. Riedel Publ. Co., 1979, p. 520. NATO Advanced Study Institute.

Translated by S. J. Amoretty