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Magnetoelastic effect in an exchange model

E. Vallejo *

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, 04510 México D.F., Mexico

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ABSTRACT

The effect of the interplay between magnetism, charge ordering and lattice distortion within a like double and super-exchange model is studied in low-dimensional systems. An important magnetoelastic effect that leads to a lattice contraction is presented in conjunction with an analytical minimization for a three-site one-dimensional model. The model is discussed in connection with the magnetism, charge ordering and the contraction of the rungs experimentally observed within the three-leg ladders (3LL) present in the oxyborate $Fe_3O_2BO_3$.

1. Introduction

In 1950, Jonker and Van Santen proposed an empirical correlation between ferromagnetism and electrical conduction in certain compounds of manganese with perovskite structure [1]. This interplay between magnetism and electronic motion was interpreted by Zener as an indirect spin coupling of incomplete d-shells via the conducting electrons (the so-called double exchange (DE) process [2]). The origin of the DE mechanism lies in the intra-atomic Hund's spin coupling J_H of localized electrons with itinerant electrons. It is the source of a variety of magnetic behavior in transition metals and rare-earth compounds. According to Hund's rule, this intra-atomic spin coupling is ferromagnetic (F) when the local spins have less than half-filled shells and antiferromagnetic (AF) otherwise. Pauli's principle also implies an AF spin coupling between the spin of conduction electrons and the spin of localized electrons in more than half-filled localized shells [3]. A similar AF coupling also occurs in Kondo systems via the so-called s–d exchange model. In this case, local spins are from a d-shell or f-shell while the conduction electrons are from s or p states. Independently of the sign of the coupling, the kinetic energy lowering, favors a F background of local spins. This F tendency is expected to be thwarted by AF super-exchange (SE) interactions between localized spins $\vec{S}_i$. This was first discussed by de Gennes [4] who conjectured the existence of canted states. In spite of recent interesting advances our knowledge of magnetic ordering resulting from this competition is still incomplete.

It has been shown recently that three-leg ladders (3LL) in the oxyborate system Fe_3BO_5 may provide evidence for the existence of spin and charge ordering resulting from a DE+SE competition [5]. The former Fe–oxyborate known as Fe–ludwigite contains subunits in the form of 3LL of Fe cations. It also presents an interesting structural and charge ordering transition at $T_c \approx 283$ K such that long and short bonds on the rungs alternate along the ladder axis [6]. As evidenced by Mössbauer studies [7,8] and X-ray diffraction [9] each rung can be viewed as three Fe^{3+} ions (*triad*) with high-spin $S = \frac{5}{2}$ local spins sharing an extra itinerant electron. Additional X-ray diffraction studies have shown an important contraction of the triads [10].

In this report, the effect of the interplay between magnetism, charge ordering and lattice distortion within a like double and super-exchange model is studied in low-dimensional systems. An important magnetoelastic effect is shown due to this interplay. An analytical minimization is presented for a three-site model. The model is discussed in connection with the magnetism, charge ordering and the contraction of the triads experimentally observed within the 3LL present in the oxyborate $Fe_3O_2BO_3$. The paper is organized as follows. In Section 2 a brief description of the model is given. Section 3 presents the results and a discussion. Finally, the results are summarized in Section 4.

* Tel.: +52 55 5623277x42561.
E-mail address: emapion@yahoo.com

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2. The model

The DE Hamiltonian is originally of the form

$$H = -\sum_{i,j;\sigma} t_{i,j}(c^{+}_{i\sigma}c_{j\sigma} + h.c.) - J_H \sum_i \vec{S}_i \cdot \vec{\sigma}_i, \quad (1)$$

where $c^{+}_{i\sigma}(c_{i\sigma})$ are the fermions creation (annihilation) operators of the conduction electrons at site i and spin σ, $t_{i,j}$ is the hopping parameter and J_H is Hund's exchange coupling. Here, Hund's exchange coupling is an intra-atomic exchange coupling between spins of conduction electrons $\vec{\sigma}_i$ and the spin of localized electrons $\vec{S}_i$. Because of the exactly half-filled shells in the Fe–ludwigite, this Hamiltonian simplifies in the strong coupling limit $J_H \to -\infty$. This limit is similar to the commonly called the DE model $J_H \to \infty$ used basically in manganite systems. Due to the high-spin configuration $S = \frac{5}{2}$ of local spins in the triads in the 3LL Fe–ludwigite, classical localized spins $\vec{S}_i \to \infty$ will be used in this work. The like DE Hamiltonian takes the well-known form

$$H = -\sum_{i,j} t_{i,j} \cos\left(\frac{\theta_{i,j}}{2}\right)(c^{+}_i c_j + h.c.). \quad (2)$$

In the Fe–ludwigite a spinless model is obtained because of the antiparallel spin orientation of itinerant electrons with respect to the spin of localized ions. $\theta_{i,j}$ is the relative angle between the classical localized spins at sites i and j which are specified by their polar and azimuth angles ϕ_i and φ_i, respectively, defined with respect to a z-axis. This axis is taken as the spin quantization axis of the itinerant electrons. The like DE+SE Hamiltonian in one dimension becomes

$$H = -\sum_i t_{i,i+1} \cos\left(\frac{\theta_i}{2}\right)(c^{+}_i c_{i+1} + h.c.) + J\sum_i \vec{S}_i \cdot \vec{S}_{i+1}, \quad (3)$$

where $\theta_{i,i+1} = \theta_i$, and J is the super-exchange interaction energy.

Finally, the effect of lattice distortion will be considered. For this goal, the complicated inter-atomic potential will be represented using classical springs to join the localized atoms. The spring forces are assumed to be linear (small displacements, Hooke's law). The hopping term changes as $t_{i,i+1} = t(1+\delta_i)$ with $-1 \ll \delta_i \ll 1$ being δ_i the i-spring displacement because of lattice distortion. Elastic energies B and V will be introduced. Similar to a boundary condition, an additional elastic energy V will be considered to avoid a large displacement of the final atom. It is important to show that this elastic energy V and the new lattice distortion proposed in this work (an extra degree of freedom) were not considered in Ref. [5]. This new lattice distortion gives the possibility to study the contraction of the triads experimentally observed using X-ray diffraction techniques in the Fe–ludwigite system [10]. The complete Hamiltonian is given by

$$H = -t\sum_i (1+\delta_i)\cos\left(\frac{\theta_i}{2}\right)(c^{+}_i c_{i+1} + h.c.) + JS^2 \sum_i \cos(\theta_i) + B\sum_i \delta_i^2 + V\left(\sum_i \delta_i\right)^2. \quad (4)$$

In the 3LL Fe–Ludwigite the distance between Fe ions along the c-axis of the ladder is 3.071 Å. Within the rungs, in the high temperature phase, this distance corresponds to 2.786 Å. These distances are not too large to avoid overlap among the 3d orbitals of the Fe ions [11]. It has been shown recently that magnetic interactions are important in Fe–ludwigite [5]. Vallejo and Avignon presented an A-phase, fully F localized spins inside the rungs and AF ones along the c-axis of the ladder. This is in qualitative agreement with the magnetic structure proposed from neutron experiments at 82 K [5,9]. In the former magnetic phase it is clear that electronic displacement along c-axis of the ladder is considerably reduced. Itinerant electrons are found basically in the triads. On the other hand, lattice distortion was also found mainly perpendicular to the c-axis therefore, in a first approximation, a three-site one-dimensional model could be used. The approach used in this paper is completely different to the used in Ref. [5]. For example, different Hamiltonian, symmetry, boundary conditions, lattice distortion and phase factor of hopping were used [5].

3. Results and discussion

Eq. (5) will be used to solve Eq. (4) for three sites and one electron.

$$\begin{pmatrix} 0 & t_{1,2} & 0 \\ t_{1,2} & 0 & t_{2,3} \\ 0 & t_{2,3} & 0 \end{pmatrix} |\Psi\rangle = Z|\Psi\rangle, \quad (5)$$

where $t_{1,2} = -t(1+\delta_1)\cos(\theta_1/2)$, $t_{2,3} = -t(1+\delta_2)\cos(\theta_2/2)$ and Z is the kinetic energy. In Eq. (5) the corresponding eigenvalues are $Z_o = 0$ and $Z_\pm = \pm\sqrt{t_{1,2}^2 + t_{2,3}^2}$. For one electron only Z_- will be considered. For Z_- the corresponding normalized eigenvector is

$$|\Psi\rangle_- = \frac{t_{1,2}}{\sqrt{2}Z_-}|1\rangle + \frac{1}{\sqrt{2}}|2\rangle + \frac{t_{2,3}}{\sqrt{2}Z_-}|3\rangle. \quad (6)$$

Charge distribution in i-site is easily obtained using the former eigenvector as $n_i = \langle i|\Psi\rangle_-\langle\Psi|i\rangle$. It is clear that charge distribution on site two is constant and always $\frac{1}{2}$. This behavior was observed using Mössbauer studies ($40\,K < T < 160\,K$) [8]. The total energy U can be obtained as

$$U = Z_- + E_{Mag} + E_{Elas}, \quad (7)$$

where

$$E_{Mag} = JS^2(\cos(\theta_1) + \cos(\theta_2)) \quad \text{and}$$
$$E_{Elas} = B(\delta_1^2 + \delta_2^2) + V(\delta_1 + \delta_2)^2.$$

An analytical minimization was made for two angles θ_1 and θ_2 and two spring displacements δ_1 and δ_2. To obtain this minimization, critical points were considered. The condition of being a critical point is either the derivative (Jacobian in vector calculus or gradient to every smooth function in the presence of a Riemannian metric or a symplectic form) vanishes, or it is not of full rank (or, in either case, the function is not differentiable). In this paper only stationary points were calculated. A stationary point is a critical point where the function stops increasing or decreasing (the derivative or the gradient are equal to zero). The condition of local minimum can be calculated using the Jacobian of the gradient. That is the Hessian matrix. The condition of local minimum is obtained for a non-degenerate critical point (the determinant of the Hessian matrix is non zero) when all eigenvalues of the Hessian matrix are positive. A local maximum is the case when all the eigenvalues are negative and it is a saddle point otherwise. For a degenerate critical point (the determinant of the Hessian matrix is zero) the test can be inconclusive.

In this paper, to calculate the stationary points and the local minimum condition, the total energy (Eq. (7)) and the first and the second derivatives are required. A total energy as a function of x_N variables $U = U(x_1, x_2, \ldots, x_N)$ is chosen. Next, it is necessary to choose a variable x_i as a starting point. The first partial derivative of the total energy as a function of x_i equals zero gives $x_{i,m}(x_1, x_2, \ldots, x_N)$ where $x_{i,m}$ is not a function of x_i. This means $\partial U/\partial x_i|_{(x_1, x_2, x_{i,m}, \ldots, x_N)} = 0$. To guaranty the first partial derivative of x_i at $x_{i,m}$ equals zero x_i must be substituted for $x_{i,m}$ in total energy. To obtain all set $\{x_{i,m}\}$ (for $i = 1$ to N) we choose another variable and follow the steps previously indicated. The point $\{x_{i,m}\}$ is a

stationary point because

$$\vec{\nabla} U|_{\{x_{i,m}\}} = \sum_{i=1}^{N} \left.\frac{\partial U}{\partial x_i}\right|_{\{x_{i,m}\}} \hat{x}_i = 0. \tag{8}$$

Local minimum condition is obtained using Hessian matrix $H(U(x_1, x_2, \ldots, x_N))_{i,j} = D_i D_j U(x_1, x_2, \ldots, x_N)$. D_m is the differentiation operator with respect to the mth argument. When all eigenvalues of the Hessian matrix are positive, a local minimum condition can be achieved.

Analytical solution of Eq. (4) implies basically four angular phases for the condition $B \neq \infty$. If the following arrangement is considered $(\theta_1, \theta_2, \delta_1, \delta_2)$ the stationary points are $(0, 0, \delta_{1,m}, \delta_{2,m})$, $(0, \theta_{2,m}, \delta_{1,m}, \delta_{2,m})$, $(0, \pi, \delta_{1,m}, \delta_{2,m})$ and $(\theta_{1,m}, \pi, \delta_{1,m}, \delta_{2,m})$. For $B \to \infty$ two stationary points were found. The point $(0, 0, 0, 0)$ and the general stationary point $(\theta_1, \theta_2, 0, 0)$. The first point is a local minimum for the condition $(1/4\sqrt{2}) > (JS^2/t)$. The second one is degenerated with the following degeneracy condition:

$$\cos(\theta_1) + \cos(\theta_2) = \frac{1}{8\left(\frac{JS^2}{t}\right)^2} - 2. \tag{9}$$

This degeneracy condition gives complete antiferromagnetism as $JS^2/t \to \infty$. The former general stationary point is a singular point or a degenerate critical point because it presents eigenvalues zero in the Hessian matrix. This solution gives a natural spin-glass behavior.

Figs. 1 and 2 present the phase diagram for two sets of typical values of the elastic energy B and the boundary elastic energy V. The value of the elastic energies B and V have been chosen to guarantee: (a) small displacements of all the atoms and (b) small spring displacements in the three-site chain.

For low super-exchange interaction energies $JS^2/t < 0.17886$ (Fig. 1) and $JS^2/t < 0.17698$ (Fig. 2) the following F local minimum solution has been found

$$\left(0, 0, \frac{1}{2\sqrt{2}\left(\frac{B}{t} + 2\frac{V}{t}\right)}, \frac{1}{2\sqrt{2}\left(\frac{B}{t} + 2\frac{V}{t}\right)}\right). \tag{10}$$

The former phase is a magnetic phase that has been observed experimentally in the triads at 82 K [9]. In this phase $\delta_1 = \delta_2$ for

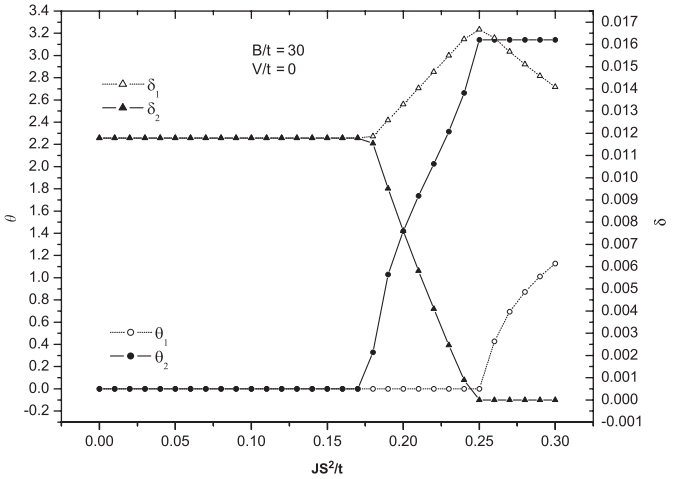

Fig. 1. Phase diagram as a function of the SE energy JS^2/t, for typical values of the elastic energy $B/t = 30$ and $V/t = 0$. Lines in this diagram represent a guide for the eyes.

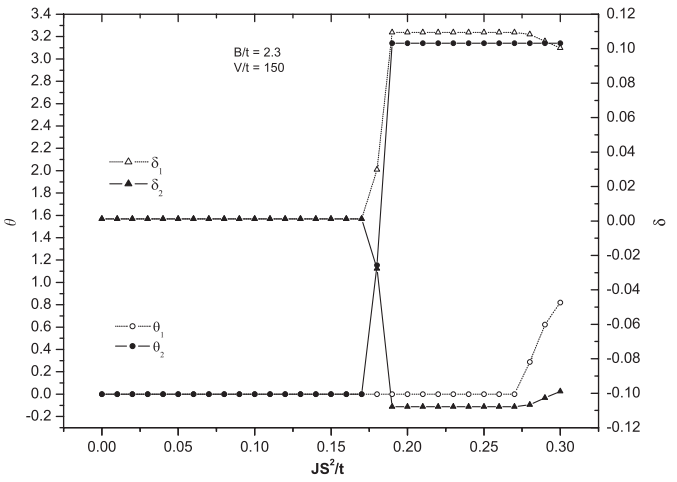

Fig. 2. Same as Fig. 1 but for the case $B/t = 2.3$ and $V/t = 150$.

symmetry reasons. Another important stationary point was found,

$$\left(0, \pi, \frac{\frac{B}{t} + \frac{V}{t}}{2\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)}, \frac{-\frac{V}{t}}{2\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)}\right), \tag{11}$$

where the local minimum condition is given by

$$\frac{B}{t} > 0,$$
$$\frac{B}{t} + 2\frac{V}{t} > 0,$$
$$\frac{2\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right) + \frac{B}{t} + \frac{V}{t}}{8\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)} > \frac{JS^2}{t} \quad \text{and}$$
$$\frac{\left(2\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right) - \frac{V}{t}\right)^2}{8\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)\left(2\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right) + \frac{B}{t} + \frac{V}{t}\right)} < \frac{JS^2}{t}. \tag{12}$$

The former conditions were obtained using the Hessian matrix and the condition that all the eigenvalues of the Hessian matrix are positive. Between $(0, 0, \delta_{1,m}, \delta_{2,m})$ and $(0, \pi, \delta_{1,m}, \delta_{2,m})$ phases it was found the phase $(0, \theta_{2,m}, \delta_{1,m}, \delta_{2,m})$ shown in Figs. 1 and 2. For high super-exchange interaction energy, phase $(\theta_{1,m}, \pi, \delta_{1,m}, \delta_{2,m})$ was obtained. For this phase the stationary point is given by

$$\theta_{1,m} = \arccos\left(\frac{(1 + \delta_{1,m})^2}{8\left(\frac{JS^2}{t}\right)^2} - 1\right),$$
$$\theta_{2,m} = \pi,$$
$$\delta_{1,m} = \frac{\frac{B}{t} + \frac{V}{t}}{-\left(\frac{B}{t} + \frac{V}{t}\right) + 8\frac{JS^2}{t}\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)} \quad \text{and}$$
$$\delta_{2,m} = \frac{-\frac{V}{t}}{-\left(\frac{B}{t} + \frac{V}{t}\right) + 8\frac{JS^2}{t}\frac{B}{t}\left(\frac{B}{t} + 2\frac{V}{t}\right)}. \tag{13}$$

Lattice contraction is given by $\delta_1 + \delta_2 \neq 0$ (Figs. 1 and 2). This contraction was obtained because of an important magnetoelastic effect given by the interplay between magnetic interactions and lattice distortion. At low temperature $T = 15$ K X-ray diffraction studies propose $\delta_2 \sim -\delta_1$ and $\delta_1 + \delta_2 \neq 0$ [10]. The X-ray studies

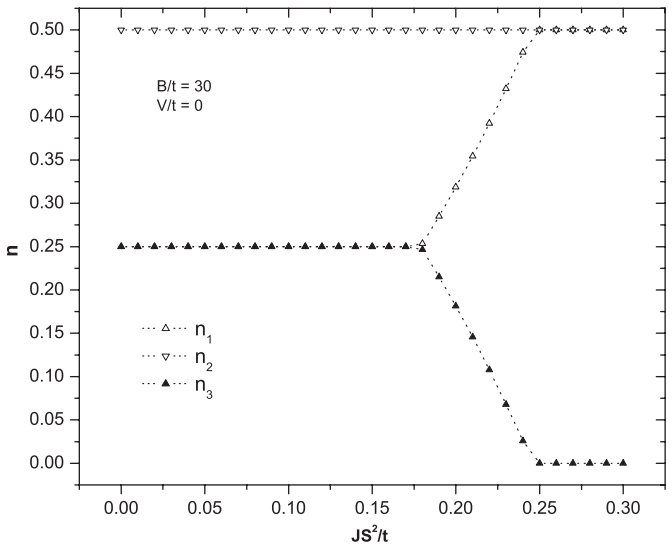

Fig. 3. Charge ordering for $B/t = 30$ and $V/t = 0$.

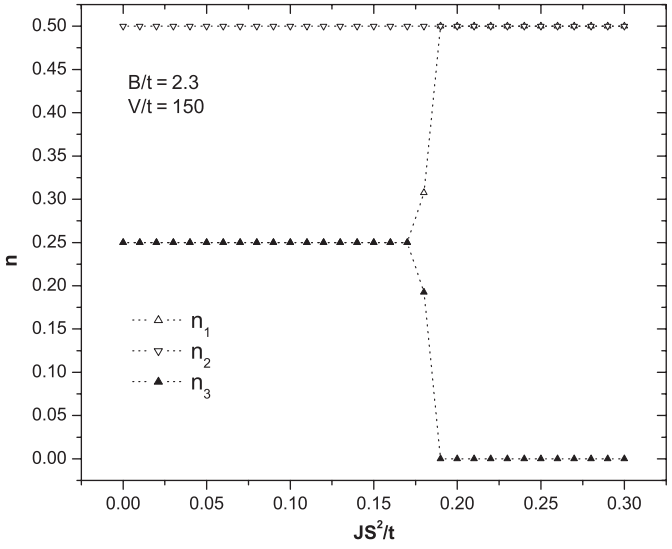

Fig. 4. Same as Fig. 3 but in this case $B/t = 2.3$ and $V/t = 150$.

are more easily improved in a $\theta_1 \neq \theta_2$ magnetic phase as shown in Fig. 2 for basically $JS^2/t > 0.177$. Fig. 2 shows that the experimental results (at low temperature) of magnetic ordering and lattice contraction can be obtained for the condition $JS^2/t \sim 0.18$. Fig. 2 also shows that for $JS^2/t = 0.18$ ($\theta_1 = 0$ and $\theta_2 = 1.15477$), a magnetic phase observed experimentally in the triads at 10 K [9]. At $JS^2/t = 0.18$ the following triads distortion ($\delta_1 \sim -\delta_2$ and $\delta_1 + \delta_2 \neq 0$) were found in a good qualitative behavior as observed by X-ray diffraction [10].

Charge distribution is presented in Figs. 3 and 4 for these two sets of values of the elastic energy B/t and V/t. Charge distribution is crucial in the Fe–ludwigite ladder so it will be analyzed in detail (see Figs. 3 and 4). Experimentally [7,8] two charge regimes were identified: (i) above T_c sites 1 and 3 are identical $n_1 = n_3 \sim 0.25-0.3$ while the central site 2 has more electrons $n_2 \sim 0.5$ and (ii) below T_c down to 74 K the charge on site 1 (the site which gets closer to site 2) increases close to the charge of site 2 which remains stable, $n_2 \approx n_1 \sim 0.5$, and at the same time the charge of site 3 decreases to $n_3 \sim 0.15$. These values [9] indicate only the tendencies since one should have $n_1 + n_2 + n_3 = 1$. However, below 74 K, two contradictory behaviors have been reported [8,9,12]. Bordet and Douvalis et al. [9,12] found that the low temperature ordering below T_c persists down to $T = 0$, while Larrea et al. [8] recovered the same charge ordering as above T_c [5]. The experimental results of Bordet at 10 K [9] are obtained in this paper for ($JS^2/t = 0.18$, $B/t = 2.3$ and $V/t = 150$). In this regimen charge ordering behavior is given by $n_2 = 0.5$ and $n_1 > n_3$. Lattice distortion is also obtained for these conditions in a good qualitative behavior as observed at 15 K by X-ray diffraction [10].

The high temperature regime of the Ludwigite system could be obtained in this model taking the F phase. A magnetic phase that has been observed experimentally in the triads at $T = 82$ K [9]. Charge ordering in this case is given by ($n_2 = 0.5, n_1 = n_3 = 0.25$).

4. Conclusions

In this paper, a three-site one-dimensional exchange model with lattice distortion was presented. An analytical solution of this model was shown to study the magnetic-charge ordering and lattice distortion properties of the triads in the 3LL $Fe_3O_2BO_3$ Ludwigite. An important magnetoelastic effect was found due to the interplay between magnetic interactions and lattice distortion. Magnetic phases, charge ordering and lattice contraction were obtained in a good qualitative behavior as observed by neutron [9] and X-ray [10] studies, respectively.

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