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JAHN-TELLER EFFECTS AND MAGNETISM

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Abstract. — Jahn-Teller instability may appear as a spontaneous distortion of the environment of an ion in a crystal (« static » Jahn-Teller effect) or as a « dynamic » effect in which there is no change in local symmetry and no splitting of degeneracy, but instead a change in the nature of the degenerate states as a result of the vibronic coupling. The resulting changes in the effective Hamiltonian which describes spin-orbit splitting, etc., as well as the response of the system to external perturbations, may be described by introducing appropriate reduction factors into the crystal-field model for the ion. A dynamic Jahn-Teller effect reduces the low-temperature magnetic susceptibility of paramagnetic systems and thus causes departures from the Curie-Weiss law. In the strong-coupling limit, small crystal strains play a crucial role in effecting the transition from dynamic to static Jahn-Teller effect.

I. Introduction. — The Jahn-Teller theorem [1] states that if a non-linear molecule or crystal defect has orbital electronic degeneracy when the nuclei are in a symmetrical configuration, then the molecule or defect is unstable with respect to at least one asymmetric displacement of the nuclei which lifts the degeneracy. Such a situation is illustrated in figure 1, for small $Q$. Taking into account the elastic energy of the lattice, which is proportional to $Q^2$, we see that the energy of the lower state reaches a minimum for the distorted configuration $Q_0$. Since the system can lower its energy by distorting to $Q_0$, the symmetrical configuration is therefore unstable with respect to this distortion. The energy difference $E_T$ is thus the energy of stabilization of the distorted configuration, and we call $E_T$ the « Jahn-Teller energy ». Energy surfaces of this type have been mapped for many different Jahn-Teller systems under a variety of assumptions by Van Vleck [2], Opik and Pryce [3], and Lieshr [4], who have found the stable configurations and calculated $E_T$ for each case.

Under suitable circumstances (to be discussed later) a crystal containing Jahn-Teller ions situated at symmetrical sites may exhibit properties (at sufficiently low temperatures) indicating that each Jahn-Teller complex has distorted spontaneously to one of its stable configurations (« static Jahn-Teller effect »). If there are several such configurations that are equivalent in energy, spectra (optical, paramagnetic or acoustic resonance, Mössbauer, etc.) of such ions are a superposition of spectra for the individual distorted configurations. At higher temperatures, thermally activated reorientation of each complex between these distorted configurations may become so rapid as to produce behavior characterising a center in which the anisotropies of the several distorted configurations have been averaged out, a type of « dynamic Jahn-Teller effect » first recognized and interpreted by Abragam and Pryce [5].

On the other hand, the Hamiltonian describing the coupling between the electronic system and the deformations of the crystal lattice represented by the $Q_i$'s has the full symmetry of the undistorted configuration, if both the electronic coordinates and the $Q_i$ are simultaneously transformed. If we treat the $Q_i$ as dynamic variables and take account of the kinetic
energy of the lattice ions, it is then clear that the energy levels of the coupled vibronic system (electrons plus lattice vibrations) must have the degeneracy required by group theory and given by the dimension of the appropriate irreducible representations of the point group of the undistorted configuration. The degeneracy of vibronic states belonging as partners to an irreducible representation of the point group of the distorted configuration therefore is not lifted by the Jahn-Teller coupling. What the Jahn-Teller coupling does is to change the nature of the degenerate states, by associating the electronic and vibrational parts of the wave function in different ways for the different vibronic eigenstates (the simple Born-Oppenheimer approximation is often not valid for these states), without changing the overall symmetry. As we will discuss below, the static Jahn-Teller effect is a limiting case of the «dynamic Jahn-Teller effect» [6-9] that describes this more general situation (1).

II. Appearance of «reduction factors» in the theory of dynamic Jahn-Teller effects. — In the crystal-field model of an ion in a crystal, the environment of the ion is treated as static, and the symmetry of the resulting crystal field is that of the site in which the ion is situated. The effective Hamiltonian that describes spin-orbit, hyperfine, and other interactions, as well as the response of the electronic system to external perturbations such as magnetic fields and applied stress, has this same symmetry. Moreover, the general form of this Hamiltonian is completely determined, apart from the values of appropriate coefficients, by the irreducible representations of the point group corresponding to the site symmetry, to which the electronic states of interest belong. Since the Jahn-Teller coupling does not change this symmetry, we see that the same form of Hamiltonian is appropriate to describe the properties of the corresponding vibronic states of the dynamically coupled system. The values of the various coefficients are however changed by the Jahn-Teller coupling, and the ratios of corresponding coefficients for the coupled system and for the electronic system in the crystal-field model (or equivalently for the coupled system in the limit in which the strength of the Jahn-Teller coupling goes to zero) define «reduction factors» which depend on the strength of the coupling. In the dynamic Jahn-Teller effect, therefore, the electron-lattice coupling manifests itself not through any change in the symmetry of the effective Hamiltonian but rather through changes in the values of these reduction factors [8]. As we will see from the following examples, such changes may be quite large, even for Jahn-Teller coupling of rather modest strength, and may therefore strongly influence such properties of the ion as its magnetic behavior.

I. ORBITAL DOUBLET IN CUBIC SYMMETRY. — The effective Hamiltonian giving the effect of interactions on an electronic orbital doublet E state (2) \( \psi_\theta, \psi_\epsilon \) transforming respectively as \( (2 \times 2 - x^2 - y^2) \) and \( \sqrt{3}(x^2 - y^2) \) in cubic (or tetrahedral) symmetry takes the general form from [9, 10]

\[
\mathcal{H} = G_1 J + G_2 A_2 + G_\theta \Omega_\theta + G_\epsilon \Omega_\epsilon,
\]

where \( J, A_2, \Omega_\theta \) and \( \Omega_\epsilon \) are orbital electronic operators transforming by the irreducible representations \([11, 12] A_1, A_2 \) and E and having matrix elements with respect to \( \psi_\theta, \psi_\epsilon \) given by

\[
\Omega_\theta = \begin{bmatrix} +1 & 0 \\ 0 & +1 \end{bmatrix}, \quad \Omega_\epsilon = \begin{bmatrix} 0 & -i \\ +i & 0 \end{bmatrix},
\]

(2)

The \( G_i \)'s in eq. (1) are functions of the components of external perturbations (magnetic field, applied stress, etc.) and of other operators (e.g. electronic and nuclear spin); \( G_1 \) is symmetric under cubic transformations of these components, \( G_2 \) belongs to \( A_2 \), and \( G_\theta, G_\epsilon \) transform as partners belonging to E. Taking account of the Jahn-Teller coupling, letting \( \psi_\theta, \psi_\epsilon \) denote the components of the vibronic doublet E ground state that arises [7] via this coupling from the electronic doublet, and defining operators \( A_2, \Omega_\theta, \Omega_\epsilon \) to have matrix elements with respect to \( \psi_\theta, \psi_\epsilon \), we find [10] then that the effect on this vibronic ground state of the operator \( \mathcal{H} \) in eq. (1) is equivalent to that of

\[
\mathcal{H}_g = G_1 J + p G_2 A_2 + p G_\theta \Omega_\theta + p G_\epsilon \Omega_\epsilon + G_\theta \Omega_\theta + G_\epsilon \Omega_\epsilon.
\]

(3)

The reduction factors \( p \) and \( q \) are given by the matrix elements of \( A_2 \) and \( \Omega_\theta, \Omega_\epsilon \) with respect to \( \psi_\theta, \psi_\epsilon \). For linear Jahn-Teller coupling with a single vibrational E mode of angular frequency \( \omega \), the behavior of these reduction factors as a function of the strength of the Jahn-Teller coupling is shown in figure 2. In

![FIG. 2. — Reduction factors p and q for the vibronic ground state in the case of the orbital doublet with linear Jahn-Teller coupling. The points are exact values, while the curves are for the approximate expressions indicated.](image)

(1) An article [9] by the author reviewing the theory of dynamic Jahn-Teller effects in electron paramagnetic resonance spectra, together with the available experimental data, is scheduled for publication in early 1971.

(2) We use interchangeably the notation \( (A_2, E, T_1, T_2) \) of Mulliken [11] and the notation \( (I, 2) \) of Bethe [12] to denote the irreducible representations of \( 0 \) or \( T_2 \).
the limit of strong coupling we have $p \to 0$, $q \to 3$. Corresponding theoretical values for $p$ and $q$ when the coupling is with more than one mode have not yet been calculated; however, experience [9] to date indicates that figure 2 gives at least qualitatively the correct behavior even in the complicated case of coupling with the continuum of lattice phonons, if a suitable average frequency is taken for the effective mode.

Applications of these general results are considered below.

2. ORBITAL TRIPLET IN CUBIC SYMMETRY. —[For an electronic orbital triplet state $\psi_2, \psi_3, \psi_4$ [transforming as $yz, zx, xy$ if the triplet is $T_2$ or as $x, y, z$ if it is $T_1$ (cubic symmetry)], the results analogous to those for the doublet may be expressed [8] as

$$\mathcal{K} = G_1 \mathcal{J} + G_2 \mathcal{F}_1 + G_3 \mathcal{F}_2 + G_4 \mathcal{F}_3 + G_5 \mathcal{F}_4 +$$
$$+ G_6 \mathcal{F}_5 + G_7 \mathcal{F}_6 + G_8 \mathcal{F}_7 + G_9 \mathcal{F}_8 + G_{10} \mathcal{F}_9,$$

(4)

$$\mathcal{K}_0 = G_1 \mathcal{J} + K(E) (G_2 \mathcal{F}_2 + G_3 \mathcal{F}_3 + G_4 \mathcal{F}_4 + G_5 \mathcal{F}_5 + G_6 \mathcal{F}_6 + G_7 \mathcal{F}_7 + G_8 \mathcal{F}_8 + G_9 \mathcal{F}_9) + K(T_1) (G_x \mathcal{F}_x + G_y \mathcal{F}_y + G_z \mathcal{F}_z).$$

(5)

Here $\mathcal{J}$ (the unit matrix) transforms as $A_1$; $\mathcal{F}_x, \mathcal{F}_y, \mathcal{F}_z$ as $E$; $\mathcal{F}_2, \mathcal{F}_3, \mathcal{F}_4, \mathcal{F}_5$ as $T_2$; and $\mathcal{F}_6, \mathcal{F}_7, \mathcal{F}_8, \mathcal{F}_9, \mathcal{F}_{10}$ (the components of an effective orbital angular momentum operator $\mathcal{F}$) as $T_1$. These operators have matrix elements with respect to $\psi_2, \psi_3, \psi_4$ given [8] by

$$\mathcal{F}_x = \begin{bmatrix} +\frac{1}{2} & 0 & 0 \\ 0 & +\frac{1}{2} & 0 \\ 0 & 0 & -1 \end{bmatrix},$$

$$\mathcal{F}_y = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{bmatrix},$$

$$\mathcal{F}_z = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{bmatrix},$$

(6)

etc.

When the Jahn-Teller coupling is with a single $E$ mode, the reduction factors are given [8] by

$$K(T_1) = K(T_2) = \exp[ -\frac{1}{2} E_T/h \omega],$$

(7)

while $K(E) = 1$. For coupling to a single $T_2$ mode, the reduction factors can be calculated by Caner and Englert [13] and have the limiting values $K(E) \to 0$, $K(T_1) \to 0$, $K(T_2) \to 2/3$.

3. EXAMPLES. — 3.1 Zeeman Splitting of a $2E$ State. — The linear coupling of the electron spin in a $2E$ state with an applied magnetic field $H$ is given [10] in general in the form of eq. (1), in cubic or tetrahedral symmetry, by

$$\mathcal{K}_s = g_1 \beta(S, H) \mathcal{J} + \frac{1}{2} g_2 \beta(3 S_z, H_z) \mathcal{H}_z +$$
$$+ \sqrt{3} S_x \mathcal{H}_z = S_y H_z) \mathcal{H}_z \mathcal{H}_z + \sqrt{3} \mathcal{H}_z \mathcal{H}_z \mathcal{H}_z.$$  

(8)

Here $\beta = (\alpha/2 mc)$ is the Bohr magneton, and $S$ the electronic spin. The two parameters $g_1$ and $g_2$ take the values $g_1 = 1 - (4 \lambda/\Delta)$, $g_2 = - (4 \lambda/\Delta)$, to the accuracy of second-order perturbation theory, for the crystal-field model of an ion in a $2E$ state [examples are $Cu^{2+}, Sc^{3+}(\text{Cd})$, $Fe^{2+}, Cr^{2+}(\text{Mg})$] split by a cubic-field splitting $^{(3)} \Delta = 10 \lambda \Delta q$, where $\lambda(L, S)$ describes the spin-orbit interaction for $2S+1D$.

For the Zeeman splitting of the vibronic $2S+1E$ ground state derived from the $2S+1E$ electronic state we accordingly find from eq. (3) that we need modify eq. (8) only by introducing the reduction factor $q$ in the terms involving $g_2$ [10]. The isotropic interaction ($g_1$) is thus not affected by the Jahn-Teller coupling, while the anisotropic interaction is reduced by up to $\sim 50 \%$. For a $4E$ state, it has been shown [9, 10] that the resulting paramagnetic resonance spectrum (at sufficiently low temperature) has two lines corresponding to the $g$-values

$$g_\pm = g_1 \pm q g_2 [1 - 3(n_s^2 n_z^2 + n_y^2 n_z^2 + n_x^2 n_y^2)],$$

(9)

where $n_x, n_y, n_z$ are the direction cosines of $H$ relative to the cubic axes, and that this result holds even when effects of random strain in the crystal are taken into account. EPR spectra exhibiting this type of dynamic Jahn-Teller effect have been identified by Coffman [14] for $Cu^{2+}$ in MgO, $g$ = 0.5, by Hübchi [15] for $Sc^{2+}$ in CaF$_2$, and SrF$_2$ ($g = 0.75$ and 0.71), by Chase [16] for $Eu^{2+}$ in CaF$_2$, and by Herrington et al. [17] for $La^{3+}$ in SrCl$_2$ ($g \approx 0.5$).

3.2 Spin-Orbit Splitting of a $2E$ State. — The spin-orbit splitting of a $2S+1E$ state, to second order in the interaction, may be expressed in the form of eq. (1) in cubic or tetrahedral symmetry as

$$\mathcal{K}_{so} = -\frac{1}{2} K \{ [3 S_x^2 - S_y S_z + 1] \mathcal{U}_x +$$
$$+ \sqrt{3} [S_y^2 - S_z^2] \mathcal{U}_y \}.$$  

(10)

For the crystal-field model and a $2S+1D$ level derived from a $2S+1D$ free ion term ($E$ below $T_2$), we take [18]

$$K = \frac{1}{2} \{ (\lambda^2/\Delta) + \rho \},$$

(11)

to include not only the spin-orbit coupling within $2S+1D$, but also the effective spin-spin interaction as given [19] by the coefficient $\rho$. A dynamic Jahn-Teller effect then modifies eq. (10) only to the extent of replacing $K$ by $K' = KqK$ in accord with eq. (3), and thus reducing the resulting splitting.

The $2E$ state of $Fe^{2+}$ or $Cr^{2+}$ is split by the interaction (10) into five uniformly spaced levels in the order $\Gamma_1$, $\Gamma_2$, $\Gamma_3$, $\Gamma_5$, $\Gamma_2$, the separation between adjacent levels being given by $K$, and the lowest level being $\Gamma_1$ if $K > 0$. Such a splitting of $2E$ has been observed [18, 19, 21] for $Fe^{2+}$ in tetrahedral symmetry in cubic ZnS, CaF$_2$, MgAl$_2$O$_4$, and some other II-VI and III-V compound semiconductors. The observed separation of these levels is somewhat smaller than the crystal-field value given by eq. (11) (in ZnS for example, 15.0 versus 25.4 cm$^{-1}$ [20]); however, this reduction may simply be due to covalent reductions in $\lambda$, and compelling evidence has not so far been developed that a dynamic Jahn-Teller effect contributes substantially to this reduction. The Jahn-Teller coupling of these levels is thus rather weak for these systems. For $Cr^{2+}$ in octahedral coordination in MgO, in contrast, the Jahn-Teller coupling is evidently so strong [22] as to

(3) The signs of the $(4\lambda/\Delta)$ terms in the expressions for $g_1$ and $g_2$ are correct if $2S+1E$ is the lower state into which $2S+1D$ splits; these signs and that of the term in $(\lambda^2/\Delta)$ in eq. (11) should be reversed if $E$ is above $T_2$. 
put the system near the limit of a static Jahn-Teller effect and thereby to produce a more complicated level structure (resulting from the proximity of an excited orbital singlet level \(5 \alpha_1\) or \(5 \alpha_2\) — see Sec. IV).

3.3 Spin-Orbit and Zeeman Splitting of an Orbital Triplet. — The Zeeman interaction for an electronic \(2S+1\) \(T_2\) or \(2S+1\) \(T_1\) state is given in the form of eq. (4) as

\[
\mathcal{K}_d = g_e \beta(L,H) + g_s \beta(S,H) \lambda,
\]

where \(g_e\) and \(g_s\) are orbital and spin g-factors which include effects of covalency. Taking account of the Jahn-Teller coupling, we find from eq. (5) that in the vibronic ground state we have

\[
\mathcal{K}_{d\text{th}} = g' \beta(L,H) + g_s \beta(S,H) \lambda,
\]

with \(g' = K(T_1) g_e\), so that the orbital part of the Zeeman interaction is thus partially quenched by the dynamic Jahn-Teller effect [8] through the appearance of the reduction factor \(K(T_1)\). The effect of the spin-orbit interaction \(\mathcal{K}_{so} = \lambda (S,H)\) on the vibronic ground state is similarly reduced, with \(\lambda\) replaced by \(\lambda' = K(T_1) \lambda\).

If we can ignore second-order corrections (see below), the spin-orbit levels arising from the vibronic ground state then have the relative energies

\[
E_{(i)} = \frac{1}{2} \lambda' J(J + 1),
\]

where we have defined an effective total angular momentum operator \(J = S + S\). The Zeeman interaction within each \(J\) level then takes the form

\[
g_s \beta(J,H)
\]

with \(g_s\) given as in the derivation of the Landé g-factor by

\[
g_s = \frac{1}{2} (g_s + g') + \frac{1}{2} \left[ (S(S + 1) - 2J) (g_s - g') \right].
\]

The above results are valid only if the over-all spin-orbit splitting of the vibronic ground state is small compared with \(\hbar \omega\), the separation of the vibronic levels. In the case of a strong spin-orbit coupling (\(\lambda > \hbar \omega\)) and a weak or moderate Jahn-Teller coupling \(\{ E_{(i)} \ll (2S + 1) \lambda\}\), the situation is more complicated, although reduction factors within the individual spin-orbit levels are still useful in describing the modifications introduced by the dynamic Jahn-Teller effect, as Ham, Schwarz, and O'Brien [23] have shown for \(Fe^{2+}\) in \(MgO\).

As a consequence of the partial quenching of the effect of certain interactions on the vibronic ground state, a dynamic Jahn-Teller effect also leads to second-order corrections [8] in this state which arise because \(\mathcal{K}_d\) in eq. (4) has matrix elements to the upper energy surface arising from the triplet in the distorted configuration of the static Jahn-Teller effect.

Reductions in spin-orbit splittings and in orbital contributions to g-factors for a number of different ions in various crystals have been attributed to dynamic Jahn-Teller effects [9]. These changes often resemble those usually associated with covalency, although the Jahn-Teller effects may be more extreme. In addition to the identification of these effects for \(Fe^{2+}\) in \(MgO\) [23], particularly striking examples are offered by various interstitial transition metal impurities \(Mn^{+}\), \(Cr^{0}\), \(Mn^{2+}\), \(Fe^{+}\) in silicon [8, 24] and by \(Tl^{3+}\) and \(V^{**}\) in \(Al_{2}O_{3}\) [25].

III. Influence of dynamic Jahn-Teller effect on magnetic susceptibility. — Applications of the theory of dynamic Jahn-Teller effects have been limited primarily to interpreting the behavior of paramagnetic impurities in crystals, particularly as to their paramagnetic resonance [9], optical absorption [26], acoustic resonance [22, 26], and Mössbauer [23] spectra. Few applications to other problems in magnetism have so far been made. One interesting recent investigation that does touch a more conventional area of magnetism is the work of Sasaki and Obata [27] on the influence of a dynamic Jahn-Teller effect on the magnetic susceptibility of a paramagnetic system, and their use of these results to explain deviations from the Curie-Weiss law in the temperature dependence of susceptibility data of Comly [28] on dilute solid solutions of \(UO_2\) in \(ThO_2\).

It is clear from the analysis that we have given above that the low-temperature paramagnetism of an ion in a state with orbital degeneracy is modified by a dynamic Jahn-Teller effect through changes in the spin-orbit splitting and through the partial quenching of the orbital contribution to the magnetic moment of the vibronic ground state. Considering for simplicity an orbital triplet state without spin, we see immediately from eq. (12-13) that, whereas the susceptibility per ion in the crystal-field model would be given by \(\chi_0 = \frac{2 g_e^2 \beta_1^2}{3 kT}\), this is modified by the dynamic Jahn-Teller effect at low temperature through the substitution of \(g'\) for \(g_e\). Moreover, we recognize from eq. (15) that the Jahn-Teller coupling induces in the ground state a temperature-independent Van Vleck-type paramagnetism. Combining these two contributions, we find then for the ratio \(\gamma(T)\) of the modified susceptibility to \(\chi_0\) in the limit as \(T \to 0\)

\[
\gamma(T) \sim (g' / g_e)^2 + 3 kT A_3.
\]
\( \gamma(0) \) is thus given by the square of the reduction factor \( K(T_c) \), while its initial slope is determined by the Van Vleck-type paramagnetism. For Jahn-Teller coupling with a single E mode, we have then from eq. (7) and (16) for \( T \to 0 \)

\[
\gamma(T) = \left[ 1 + 2(kT/h\omega) G(3E_{JT}/h\omega) \right] \times \exp(-3E_{JT}/h\omega). \tag{19}
\]

In this case of a triplet with Jahn-Teller coupling to an E mode, Sasaki and Obata [27] have obtained an exact expression for \( \gamma(T) \), valid at all temperatures, that takes account of thermally excited occupation of higher vibronic levels as well as of the ground state (4). Their result may be shown to agree with eq. (19) in the limit as \( T \to 0 \). For more complicated Jahn-Teller problems, such as those including spin, for which an exact expression may be impossible to obtain, we may nevertheless determine the limiting value of \( \gamma(T) \) and its slope from a procedure like that which led to eq. (18-19). The high temperature limit of \( \gamma(T) \) is unity, whatever the form of the Jahn-Teller coupling.

It is of interest to compare the behavior of the susceptibility for a dynamic Jahn-Teller effect, as given by Sasaki and Obata's expression for \( \gamma(T) \), with the result one obtains by imposing a tetragonal distortion in the crystal-field model, letting the splitting between the lower state of the split triplet and the two higher states be \( 3E_{JT} \), and taking the orientation of the axis of the distortion to be distributed at random between the \( x \), \( y \), and \( z \) axes. This comparison is shown in figure 3. The greatest difference is of course at low temperature, where \( \gamma(0) = 0 \) for the model with the static distortion, in contrast to the non-zero value obtained for a dynamic Jahn-Teller effect if the ratio \( E_{JT}/h\omega \) is not too large. At higher temperature the behavior is similar; this is particularly so for the larger values of \( E_{JT}/h\omega \), as we would expect because we then

\[ \gamma(T) \sim \left[ 1 + 2(kT/h\omega) G(3E_{JT}/h\omega) \right] \times \exp(-3E_{JT}/h\omega). \]
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