Tunneling Splitting of Jahn-Teller Ions in Oxides

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The magnitude of tunneling splitting, 3Γ, that governs decoherence in quantum systems under symmetric potentials, is frequently unknown. Using first-principles calculations, we have obtained 3Γ for a number of $E \otimes e$ Jahn-Teller impurities in solids. Calculated values span 6 orders of magnitude on passing from KCl:Ag^{2+} to MgO:Cu^{2+}. Values associated with Cu^{2+}- and Ag^{2+}-doped MgO are 2 orders of magnitude larger than those previously assumed and consistent with the existence of a dynamic Jahn-Teller effect. The origin and enhancement with pressure of these high 3Γ values is discussed in detail.

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Tunneling is well recognized as one of the most fundamental but intriguing quantum mechanical phenomena from the dawn of quantum mechanics, and it actually plays a crucial role in all branches of science from elementary particle physics to biology [1]. In later years, there has been great interest in solid-state applications of quantum tunneling through symmetric multiwell potentials, including the possibility of creating workable quantum computers [1,2]. The formation of coherent states by superposition of the degenerate localized states at the equivalent minima is crucial in these problems. These states are separated by a small energy gap called tunneling splitting. Despite the key role played by tunneling splitting in decoherence phenomena, its magnitude is frequently unknown [1]. This is the case of the dynamic $E \otimes e$ Jahn-Teller effect (JTE) in solid-state systems [3,4], a field that has received a great deal of attention in the last few years. As reviewed by Englman [4], dynamic JTE systems show, on one hand, a strong entanglement between electronic and vibrational degrees of freedom [5] that could be exploited in the nascent field of quantum computation [2,5]. Also, the dynamic JTE has been shown to play a very important role in the colossal magnetoresistance of the manganites [6] and the superconductivity of some systems, like the fullerites [7]. Moreover, new developments regarding the electron-vibration coupling in copper oxide high-temperature superconductors [8] are attracting much attention, in particular, the bipolaron JTE model [9]. In the dynamic $E \otimes e$ JTE, the interaction between the degenerate vibrational states at the three equivalent conformations present in the wave function involves the entanglement with two electronic states. The coherence of this system can however be destroyed by the strain field produced by defects inevitably present in every real crystal. This leads to what is called a static JT, in which the system is trapped in a single minimum (Fig. 1), and then the rich physics inherent to electron-vibration coupling, including Berry phase [10] and nonadiabaticity [8], is lost.

The existence of a dynamic $E \otimes e$ JTE was first observed experimentally in the electron paramagnetic resonance (EPR) spectrum of Cu^{2+}-doped MgO [11] at $T = 1.2$ K after its theoretical prediction by Bersuker [12], who proposed that the three localized wave functions at each of the wells associated to the $E \otimes e$ JT problem would interact and give rise to E (doublet) and A_1 (singlet) levels separated by the tunneling splitting, 3Γ (Fig. 1). This spectrum constitutes the fingerprint of an E vibronic orbital doublet and thus exhibits a *cubic* angular pattern and not a tetragonal one characteristic of a static JTE [3,13]. The existence of coherent tunneling was later confirmed for a few sys-

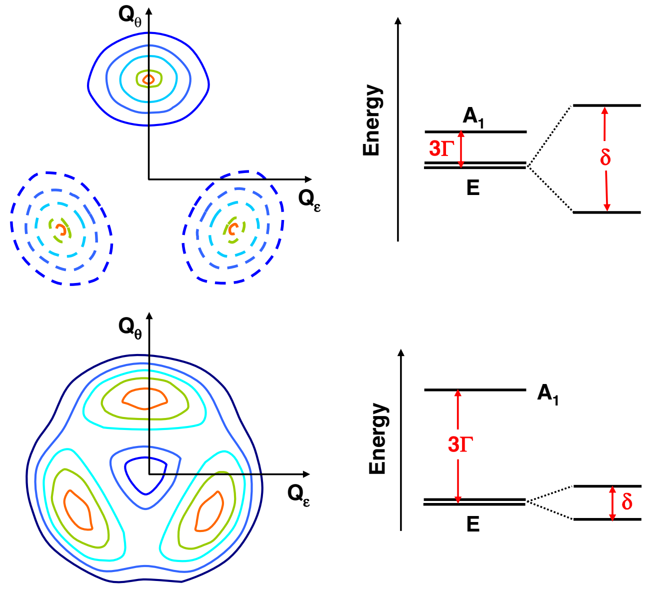

FIG. 1 (color online). Illustration of the nuclear density for the cases of static (up) and dynamic (down) $E \otimes e$ JTE. In the static case, the system is trapped into one (continuous line) of the three initially equivalent JT minima (slashed lines) due to the strain field δ. In the dynamic case, the nuclear density has a nearly equal contribution from each of the wells because $3\Gamma \gg \delta$.

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tems [13–15] like MgO:Ag^{2+} [13,14], but up to now it has *never* been found for d^9 or d^7 ions in cubic halides with octahedral coordination [3] or in SrO [13] all of them displaying a static JTE. The different behavior of these systems makes them ideal models to understand the different factors influencing vibrational JT tunneling in solid-state problems and, in particular, in oxides as well as its order of magnitude.

Despite that solid evidence of a dynamic JTE in MgO:Cu^{2+} was found more than 40 years ago and recently confirmed [16], there is still a key question which has not yet been answered: why such a phenomenon is observed *exclusively* for MgO:Cu^{2+} or MgO:Ag^{2+} and not for systems like Ag^{2+}-doped KCl or NaCl:Rh^{2+} [3,17]. According to Ham [18], the dynamic or static nature of the JTE is determined by the comparison of the tunneling splitting with the tetragonal splitting coming from random strains, δ, which is sample dependent. The condition $3\Gamma \gg \delta$ favors a dynamic JTE; otherwise, the system will be frozen along one particular deformation (Fig. 1). Even though 3Γ is such an important quantity, very little is known about its value as can be deducted from a recent and thorough review on the JTE [3]. Most authors *estimate* 3Γ to be around a few cm^{-1} [2,10,13–16,18] consistent with other heavy-particle tunneling values like the one, for example, in ammonia (1.26 cm^{-1}). In this Letter, we carry out the calculation from first-principles of the tunneling splitting for a number of $E \otimes e$ JTE systems and show that the values associated to Cu^{2+} and Ag^{2+} impurities in MgO are 2 orders of magnitude larger than those previously assumed.

Two main steps are necessary for properly calculating 3Γ. In the first step, the distortions associated with the three equivalent adiabatic minima, the JTE energy, E_{JT}, and the barrier between two minima, β (Fig. 2), are determined by means of *ab initio* calculations. If $Q_\theta = \rho\cos\varphi$ and $Q_\varepsilon = \rho\sin\varphi$ are the two normal coordinates of the e mode that transform, respectively, like $3z^2 - r^2$ and $x^2 - y^2$, the energy surface minima are described by $\{\rho = \rho_0, \varphi = 0, \pm 2\pi/3\}$ if the octahedron is elongated. In this work, values of ρ_0, E_{JT}, and β have been derived by means of the Complete Active Space Self Consistent Field method corrected by second order perturbation theory (CASPT2) first-principles method that includes most of the electron correlation energy and usually yields excellent results [19]. We employed the MOLCAS 6.2 program suite [19] to perform the calculations. The technical details on basis-sets, fitting of energy surfaces and embedding of the cluster, are thoroughly described in our previous works [20]. The main differences with previous calculations are an increased cluster size and that full geometry optimizations are carried out for the complex. Our results, shown in Table I, are in good agreement with previous density functional theory (DFT) [20] and CASPT2 calculations [20,21] and only show minor improvements. Moreover, the values of E_{JT} and β in Table I are consistent with all the available experimental information derived for KCl:Ag^{2+}, NaCl:Ag^{2+}, and NaCl:Rh^{2+} which display a static JT effect [3,17,20,22].

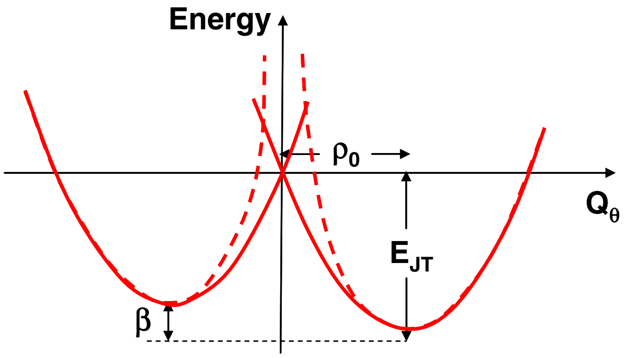

FIG. 2 (color online). Plot of a cross section of the adiabatic energy surface of a $E \otimes e$ JT system along the Q_θ coordinate ($Q_\varepsilon = 0$) showing the meaning of ρ_0, E_{JT}, and β parameters (bold line). The effective potential when the nonadiabatic centrifugal-force for $m = 1/2$ is taken into account is shown with a dashed line.

Once ρ_0, E_{JT}, and β have been determined, the 3Γ value is obtained by diagonalizing the vibronic Hamiltonian [3]

$$H_V = \frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial Q_\theta^2} + \frac{\partial^2}{\partial Q_\varepsilon^2}\right) - V(Q_\theta\hat{\sigma}_z + Q_\varepsilon\hat{\sigma}_x) + \frac{1}{2}K(Q_\theta^2 + Q_\varepsilon^2) + G\{(Q_\theta^2 - Q_\varepsilon^2)\hat{\sigma}_z + 2Q_\theta Q_\varepsilon\hat{\sigma}_x\} \tag{1}$$

where M denotes the ligand mass and the electronic operators $\hat{\sigma}_z$ and $\hat{\sigma}_x$ act only in the E subspace described by the Φ_j ($j = \theta, \varepsilon$) electronic wave functions. In this basis, $\hat{\sigma}_z$ and $\hat{\sigma}_x$ are represented by Pauli matrices. The constants V, K, and G are the linear JTE coupling, elastic, and warping terms, respectively, and are derived from the values of ρ_0, E_{JT}, and β obtained through the adiabatic electronic structure calculations carried out in the first step. In order to obtain the vibronic levels associated with (1),

TABLE I. Results from CASPT2 *ab initio* calculations for several $E \otimes e$ JTE systems and their corresponding 3Γ values calculated using Eq. (1). A negative value of β indicates that the octahedral complex is predicted to be compressed while a positive one indicates an elongated complex.

System	ρ_0 (Å)	E_{JT} (cm^{-1})	β (cm^{-1})	3Γ (cm^{-1})
MgO:Cu^{2+}	0.0875	445	-11	234.79
CaO:Cu^{2+}	0.1288	567	-25	130.53
MgO:Ag^{2+}	0.1025	685	-16	200.31
CaO:Ag^{2+}	0.225	977	-136	29.43
NaCl:Ag^{2+}	0.3256	1623	599	0.49
KCl:Ag^{2+}	0.5196	2363	1024	5×10^{-4}
NaCl:Rh^{2+}	0.3200	1832	511	0.50

H_v is diagonalized within the basis set given by

$$\Psi_{j;l,n} = \Phi_j \chi_l(Q_\theta)\chi_n(Q_\varepsilon). \tag{2}$$

Here, $\chi_1(Q_\theta)$ and $\chi_n(Q_\varepsilon)$ $(l, n = 0, 1, \ldots, L)$ are harmonic oscillator wave functions. Our calculations have been carried out using up to $L = 50$, converging the energy levels down to 10^{-6} cm^{-1}.

Our main results are collected in Table I for a series of $E \otimes e$ JT systems. The values of ρ_0, E_{JT}, and β for MgO:Cu^{2+} are comparable to those derived in previous calculations [20,21]. The value $\rho_0 = 8.75$ pm implies a small distortion of the ligand octahedron leading to $R_{eq} - R_{ax} = 7.4$ pm, where R_{eq} and R_{ax} stand for the equatorial and axial metal-ligand distances. The average value $R_0 = (2R_{eq} + R_{ax})/3$ has been found to be equal to 214 pm. It is worth noting that in the extended x-ray-absorption fine structure spectroscopy (EXAFS) measurements by Hildebrand and Martin [23] and Asakura *et al.* [24], the system MgO:Cu^{2+} appears to be cubic, even though the tetragonal distortion was thoroughly sought after. Hildebrand *et al.* [23] found $R_0 = 211$ pm, while similar values have also been reported from EXAFS measurements for Ni^{2+} and Co^{2+} impurities in MgO [25]. While values $R_{ax} = 255$ pm and $R_{eq} = 218$ pm have recently been reported for MgO:Cu^{2+} [26], we find that they are in strong contradiction with other experimental [23–25] and calculated [20,21] geometries, including ours.

The calculated 3Γ values for $E \otimes e$ JT systems span 6 orders of magnitude on passing from KCl:Ag^{2+} to MgO:Cu^{2+} which exhibits the highest value among the studied systems. These changes are indicative of the magnitude of the JT distortion, which in the stiffer lattices is smaller, favoring large 3Γ values, and, in the softer ones, is much larger favoring stronger barriers and negligible tunneling splittings. It is worthwhile to stress that even recently, it has been conjectured that 3Γ would be around 5 cm^{-1} for MgO:Cu^{2+} [14,16,18]. This figure is however not easy to accept if we take into account that δ values are known [18] to be of the order of 10 cm^{-1}, and the JTE in MgO:Cu^{2+} is dynamic. Therefore, the condition $3\Gamma \gg \delta$ can hardly be fulfilled assuming $3\Gamma \approx 5$ cm^{-1}. By contrast, such a requirement is fully compatible with the values $3\Gamma = 235$ and 200 cm^{-1} derived in the present calculations (Table I) for MgO:Cu^{2+} and MgO:Ag^{2+}, respectively. Although both values are *2 orders of magnitude* higher than those given in previous estimations, they are fully consistent with the existence of coherent tunneling in both systems, a fact well corroborated by EPR spectra taken at 1.2 K. From the EPR measurements on MgO:Cu^{2+}, it was estimated a ratio $\delta/3\Gamma$ around 0.1 which, according to Table I, would imply a δ value around 20 cm^{-1} for the sample studied by Reynolds *et al.* [14]. At the same time, the calculated 3Γ values for Ag^{2+}- or Rh^{2+}-doped alkali chlorides (Table I) are all smaller than 1 cm^{-1} and thus support beyond any doubt that quantum coherence should be destroyed by random strains. This conclusion is also in agreement with low temperature EPR data [3,17] showing that the local symmetry is D_{4h}.

It is worth noting that there is a significant reduction of the 3Γ values when MgO is replaced by CaO as host lattice. As shown in Table I, $3\Gamma = 130$ cm^{-1} for CaO:Cu^{2+} while a lower value ($3\Gamma = 29$ cm^{-1}) is found for CaO:Ag^{2+}. It should be pointed out that the EPR spectra due to CaO:Cu^{2+} also correspond to a ^2E doublet though the lines are much more broadened by random strains than in the case of MgO:Cu^{2+} [13,14]. By contrast, in the case of CaO:Ag^{2+}, where the calculated 3Γ value is reduced by a factor of 4.5 with respect to that for CaO:Cu^{2+}, the EPR spectra already displays a static JTE. This result thus suggests that even if $\delta/3\Gamma$ is down to around 0.4, coherence can be destroyed by random strains. First calculations including the effect of a strain on the JTE system [27] support this conclusion.

Let us now focus on the actual origin of the high 3Γ value found for MgO:Cu^{2+}. As shown in Table I, the barrier, β, between two adiabatic minima is practically negligible for MgO:Cu^{2+}, a surprising circumstance whose microscopic origin has previously been discussed in detail [20]. Because of this relevant fact, the potential energy in the Hamiltonian H_v is essentially independent on the φ coordinate, and thus the system can rotate constrained to a circle of radius ρ_0. The kinetic energy associated with such a motion is simply given by

$$E_m = \frac{\hbar^2}{2M\rho_0^2} m^2. \tag{3}$$

It should be stressed now that when warping is negligible in the $E \otimes e$ JTE, the total wave function of lowest *vibronic* states is essentially given by

$$\begin{aligned} |\Psi\rangle &= |\phi_{el}\rangle \chi(\rho - \rho_0) e^{im\varphi}; \\ |\phi_{el}\rangle &= \cos\frac{\varphi}{2}|x^2 - y^2\rangle + \sin\frac{\varphi}{2}|3z^2 - r^2\rangle. \end{aligned} \tag{4}$$

As when $\varphi \rightarrow \varphi + 2\pi$, the electronic wave function $|\phi_{el}\rangle \rightarrow -|\phi_{el}\rangle$, this requires that the rotational quantum number m, involved in the nuclear part of Eq. (4), has to be *half integer* and thus the lowest vibronic state corresponds to $m = \pm\frac{1}{2}$ [3] Accordingly, the kinetic energy for the ground vibronic doublet [Eq. (3)] dominates over the warping term provided $\hbar^2/8M\rho_0^2 \gg |\beta|$. In such a case, 3Γ can simply be approximated by $\hbar^2/M\rho_0^2$. Using now $\rho_0 = 8.75$ pm and the mass of the ^{16}O isotope, this simple expression already gives $3\Gamma = 272$ cm^{-1} for MgO:Cu^{2+} which is not far from the figure derived from present calculations (Table I). In comparison with other systems described in Table I, MgO:Cu^{2+} exhibits the lowest ρ_0 value, a fact which, as it was previously pointed out [20], partially reflects that MgO is the stiffest host lattice among those considered in Table I. A decrease of ρ_0 not only favors a reduction of the barrier, but it also enhances the value of the $\hbar^2/M\rho_0^2$ quantity. Both facts qualitatively explain the large 3Γ reduction on passing from MgO:M^{2+} to CaO:M^{2+} ($M =$ Cu, Ag). It turns out from the present analysis that in MgO:Cu^{2+}, all conformations described by $\{\rho = \rho_0, \varphi\}$ have essentially the same probability. Thus, at variance with what happens in the case of a static JT effect, EXAFS experiments on systems like MgO:M^{2+} ($M =$ Cu, Ag) can hardly show a particular distortion among all possible conformations. EXAFS results by Hildebrand and Martin [23] on MgO:Cu^{2+} are consistent with this view.

The existence in the $E \otimes e$ problem of a practically free rotation along the $\rho = \rho_0$ circle if ρ_0 is small enough is somewhat similar to what is found in a crystalline compound when the lattice parameter, a, is reduced. In that case, when a is sufficiently small, the kinetic energy of an electron dominates over the potential one, and valence electrons just behave as free particles of a metal.

The present results strongly suggest that the existence of coherent tunneling would be favored by application of hydrostatic pressures, since a reduction of ρ_0 is expected in that case. In this regard, it is important to note that the dynamics induced by the JTE are different from the dynamics associated to non-JTE distortions (due to, for example, the pseudo JTE [3]) because of their strong nonadiabaticity and the presence of a Berry phase [3,10]. As shown above, the angular momentum quantum number, m, [Eq. (3)] is half integer, leading to a non-null centrifugal contribution [3] for *any* value of m (see Fig. 2). While in usual off-center systems, like in KCl:Li^+ or ferroelectrics [3], the application of pressure simply destroys the distortion and the tunneling associated with it, in JTE systems, the centrifugal term goes as $1/\rho^2$ and is never perturbative with respect to the elastic energy. As a consequence, the nuclear density must be zero for $\rho = 0$ at difference with usual distortions. Thus, JTE systems are strongly resistant to pressure, and tunneling, entanglement, and nonadiabatic effects are enhanced by pressure. This can be seen in our calculations since a small reduction of a 3% in the MgO lattice parameter, corresponding with a pressure of 14 GPa, increases the value of 3Γ in MgO:Cu^{2+} from 230 cm^{-1} to 275 cm^{-1}. Along this line, it is significant that the highest Tc in cuprate superconductors is achieved at high-pressure [28]. This effect could also be exploited to increase the temperature at which a quantum computer based on JTE-dynamics would work [5]. Further work on these issues is being carried out.

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