Phosphorescence Microwave Double Resonance Spectroscopy in Ionic Solids and Its Application to Coherent Jahn-Teller States in *F* Centers of CaO

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We demonstrate the use of phosphorescence microwave double resonance (PMDR) in ionic solids applied to the dynamic Jahn-Teller effect in *F* centers of CaO. A tunnel splitting ($\Delta = 2.1\ \mathrm{cm}^{-1}$) is obtained and Jahn-Teller states are coherent in zero field at least 10^3 times longer than the stochastic limit, and possibly as long as the lifetime of the centers. This is demonstrated by showing the loss of coherence by small Zeeman perturbations on the PMDR spectrum.

Phosphorescence microwave double resonance spectroscopy (PMDR)[1] is a technique which has allowed much of the kinetic information regarding the populating routes and decay channels of electronic-excited-state energy into triplet states to be obtained easily and routinely in molecular solids. It is a zero-field spectroscopic technique based on optically detected magnetic resonance (ODMR) in high field[2,3] which was subsequently extended to zero field.[4] PMDR monitors the individual vibronic bands in emission and measures the quantitative changes induced in the emission by a microwave field resonant with the zero-field splittings. Because of the sensitivity of photon detection, it is capable of measuring properties on as few as 10^4 excited states depending upon the details of the radiative channels being monitored. Applications of PMDR have been so extensive in the last four years that to do justice to the contributors would require an extensive reference list. A recent thorough review of this field, however, has been written by Kwiram.[5]

Although many properties of ionic solids[6] are different from molecular solids, the basic features of excited *F* centers are similar to excited triplet states, particularly in zero field. For example, if one takes D_{4h} as the point symmetry of *F* centers of CaO, there is a one-to-one correlation of the individual spin sublevels of the *F* center in zero field with $^3\mathrm{B}_{1u}$ molecular excited triplet states.[7] Many excited triplet states in molecular crystals have been unequivocally[8] established through PMDR in $^3B_{1u}(\pi, \pi^*)$ states. We expect therefore that the dynamics of populating and depopulating excited centers can be elucidated in ionic solids as simply and easily as in triplet states in molecular solids. Moreover, PMDR has been recently used to establish coherence in excited triplet excitons[9] and spins[10] in molecular solids, and one might expect the same could be accomplished in ionic and semiconducting crystals having accessible triplet states.

In this paper we will (a) demonstrate zero-field PMDR in *F* centers of CaO, (b) illustrate how the methods can be used to extract tunnel splittings from the zero-phonon origin in CaO, and finally, (c) determine a minimum coherence time for the split Jahn-Teller states and shed some light on how the coherence is lost, and its relationship to the dynamic Jahn-Teller effect.[11a,11b]

To illustrate the principles, we begin with a consideration of the *F* centers in the cubic $^3T_{1u}$ state subject to a dynamic Jahn-Teller effect[11a,11b] through coupling with an e_g mode.[12]

Various perturbations are capable of lifting this degeneracy; however, the degeneracy is lifted *completely* only in case the projections of the perturbing vector that couples to the triplet system show orthorhombic symmetry, e.g., if $e_\epsilon = (\sqrt{3}/2)[e_{11} - e_{22}]$ is nonzero[11b] and all other components, e_{ij}, of the strain tensor are zero, then the energies of the $\psi(+--+)$ and $\psi(-+-)$ states are shifted by $+\Delta$ and $-\Delta$, respectively. In this instance $\psi(+++)$, $\psi(+-+)$, and $\psi(-+-)$ diagonalize the total Hamiltonian. Additionally, it can be shown[7] that the zero-field splitting parameters in the electron spin Hamiltonian differ for the different $\psi(lmn)$ states because the tunnel splitting Δ causes an explicit (lmn) dependence of the spin-orbit contributions to the zero-field splitting. Similar arguments have been applied to the zero-field splittings of coherent Frenkel-exciton k states and used to elucidate properties of coherent wave packets.[9] It is important to note that $\psi(lmn)$ are *stationary* solutions to the Schrödinger equation in the absence of a relaxation Hamiltonian; hence, the states $\psi(lmn)$ can be considered *coherent* in the absence of some relaxation.

Coherence and the promoting mode[11a,11b] responsible for the dynamic Jahn-Teller effect in F centers have been considered, and the optical detection of F-center EPR in CaO in high and intermediate fields has been observed.[12] However, the observation of the dynamic Jahn-Teller effect has still eluded investigation.

To demonstrate the power of applying zero-field PMDR to ionic solids, Fig. 1 diagrammatically illustrates the problem while Figs. 2(a)–2(i) present the experimental data on the F center in CaO. These include the emission [2(e)] and PMDR spectra in zero field [2(f), 2(g)] and 50 G [2(h), 2(i)] at 1.5°K monitoring the zero-phonon[13] origin, (0, 0), in addition to the ODMR results at 0 [2(a)], 10 [2(b)], 20 [2(c)], and 50 [2(d)] G.

CaO crystals were prepared by additive coloration[14] and had an F center concentration of 5×10^{17} centers/cm^3. CaO was excited with the 3100-Å line of a 100-W high pressure Hg-Xe lamp. The zero-phonon[13] origin was isolated by a 1-m spectrometer. Other experimental details are essentially the same as reported earlier[8] except that changes in microwave-induced phosphorescence was phase detected at 105 Hz.

The results from these experiments can be understood as follows. Two zero-field transitions, hereafter labeled ω_1 and ω_2, are seen at 1675.5 and 1696.7 MHz, respectively [cf. Fig. 2(a)]. The PMDR spectrum of ω_1 [2(f)] yields a spectrum where the maximum in the phosphorescence emission is coincident with the maximum in the PMDR spectrum. On the other hand, the PMDR spectrum of ω_2 [2(g)] yields two peaks symmetrically split from ω_1 by about 4.2 ± 0.2 cm^{-1}. Moreover, the microwave-induced change in phosphorescence increases for ω_1 and decreases for ω_2 indicating a difference in the populating and decay rates for the three stationary Jahn-Teller states. In the zero-field ODMR spectrum [2(a)] the difference between the zero-field splitting in the $^3\psi(+++)$ and $^3\psi(\pm\mp\pm)$ states is 21 MHz because of selective spin-orbit coupling contributions to the zero-field splittings. The difference in their respective optical PMDR spectra amounts to 2.1 ± 0.1 cm^{-1}. This means that the tunnel splitting is $\Delta=2.1\pm0.1$ cm^{-1}.

The fact that all three splittings are resolved in the PMDR spectrum [2(f), 2(g)] means that the

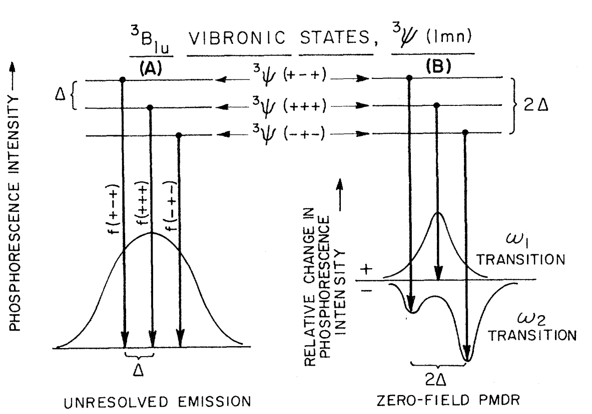

FIG. 1. Schematic diagram of the principles used to elucidate the dynamic Jahn-Teller effect using PMDR.

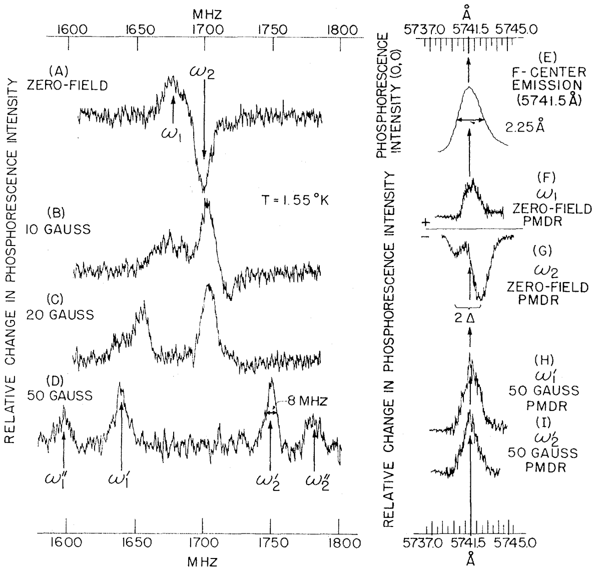

FIG. 2. ODMR results (a)–(d) and PMDR spectra (b)–(i) in F centers of CaO.

Jahn-Teller states are coherent in zero field. A minimum coherence time can be established from exchange theory[15] which states that intermediate exchange is given by the condition $(\omega_2 - \omega_1)\tau \sim 1$. The coherence time, τ, in CaO is therefore longer than 5×10^{-8} sec. Thus, coherence persists in the Jahn-Teller states in zero field at least 6×10^3 times longer than that associated with the stochastic "random" incoherent limit, which is given by $(2\Delta)^{-1}$ sec. The coherence is associated with only one point in the full-time correlation function,[7] namely 5×10^{-8} sec.

From another point of view, if we assume that the linewidths at half-height in the ODMR spectrum [2(a)], corresponding to ω_1, 15.0 MHz, and ω_2, 10.7 MHz, are homogeneous, a minimum coherence time of 7×10^{-7} sec for the ${}^3\psi(+++)$, and 1×10^{-7} sec for the ${}^3\psi(+--+)$ and ${}^3\psi(-+-)$ can be obtained. In this case the coherence is persistent at least 6×10^2 and 4×10^3 times the stochastic limit for the ${}^3\psi(+++)$ and ${}^3\psi(\pm\mp\pm)$ states, respectively, at 10^{-7} sec in the time correlation function. Since CaO contains no nuclei that have nuclear spins, apart from ^{43}Ca (0.13%), it is unlikely that hyperfine interactions (an inhomogeneous term) would be important. The coherence time could be longer however if small crystal strains result in ODMR line broadening. This is not the case, since as one increases a dc magnetic field, applied at approximately 45° to the (100) face, the ODMR spectra appear intermediately exchanged, *not at zero field,* but at about 10 G [2(b)] and the microwave-induced change in phosphorescence associated with ω_1 changes sign completely by 20 G [2(c)]. This is simply because by 20 G the Jahn-Teller states are in exchange on a time scale faster or comparable to the excited-state lifetimes[13] (3×10^{-3}) of the ${}^3\psi(lmn)$ states.

Because of the optical resolution of the PMDR spectrum in zero field [2(e), 2(f)], *it is quite possible that the coherence time could approach the lifetime of the centers in zero field,* and that the coherence is lost rapidly with small Zeeman energies (0–20 G). The loss of coherence could also be decaying via some other channel, apart from scattering between the ${}^3\psi(lmn)$ states themselves. The loss of coherence via Zeeman terms, however, can be established. By 50 G the two electron spin transitions that are degenerate in zero field because of D_{4h} symmetry are clearly resolvable [2(d), ω' and ω'']. Furthermore, the system is in the fast-exchange limit since the lines associated with ω_1' and ω_2' are narrower. Figure 2(d) shows that ω_1' and ω_2' have linewidths at half-heights of 8 MHz. Finally a PMDR on ω_1' and ω_2' at 50 G [2(h), 2(i)] confirms that under the influence of a small Zeeman field, which mixes the zero-field spin eigenfunctions of the three states, ${}^3\psi(+++)$, ${}^3\psi(+-+)$, and ${}^3\psi(-+-)$, the states are no longer coherent on a time scale of 10^{-3} sec. This is established by the fact that the maximum in the PMDR [2(h), 2(i)] and the maximum in the phosphorescence emission [2(e)] are coincident due to fast exchange relative to the F-centers excited-state lifetime (approximately 3×10^{-3} sec) for both Zeeman-split sites.

In summary, we have demonstrated (a) the first PMDR in ionic solids, specifically, PMDR in the triplet F centers of CaO; (b) obtained the Jahn-Teller splittings for the center; (c) shown that the states are coherent for times at least 10^3 exceeding the stochastic limit, and possibly approaching the lifetime of the excited states in zero field; and finally (d) suggested that the mixing of the spin eigenfunctions of ${}^3\psi(+++)$, ${}^3(+--+)$, and ${}^3\psi(-+-)$ is responsible for the loss of coherence as a function of field, because it introduces new off-diagonal matrix elements in the zero-field basis.

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Approximate Renormalization Group Based on the Wegner-Houghton Differential Generator*

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We give an approximate renormalization-group formulation which parallels that of Wilson. The group generator represents the momentum-independent limit of the differential generator of Wegner and Houghton. The eigenfunctions near the Gaussian point are computed for all spin dimensions n and lattice dimensions d, including $d = 2$. The nontrivial fixed-point Hamiltonian in dimensions near $d = 2\Theta/(\Theta - 1)$, together with the eigenvalues near that nontrivial fixed point, are found explicitly to first order in $\epsilon_\Theta \equiv \Theta(2-d)+d$ for *all* values of n and the order Θ. Odd-dominated Ising systems and corresponding expansions in $\epsilon_{\Theta-1/2}$ are also treated.

The renormalization-group approach to the study of critical phenomena has had great initial success.[1-2] The renormalization group embodies in concrete mathematical form the scaling notions of Kadanoff[3] and provides a framework for explicit calculation. These calculations have usually been done by perturbative expansions, in analogy with similar problems in quantum field theory. All the difficulties of field theory have been incorporated into critical-phenomena calculations as well; the calculation of thermodynamic quantities involves complicated Feynman diagrams and divergent integrals.

Even in those cases where field-theoretic difficulties are not encountered, the perturbation techniques have been "brute force" in nature. For example, the calculation of critical-point exponents for higher-order[4] critical points has been hampered by the rapid increase of the number of equations which contribute.[5]

Many renormalization-group problems can be simplified by revising the perturbative techniques to conform as closely as possible to the structure of the renormalization group itself. It was noted by Wegner[6] that the eigenfunctions of Wilson's approximate renormalization group (when linearized around the Gaussian point[2]) are related to Laguerre polynomials. However, this observation has hitherto not been fully exploited. Here we show that by utilizing the structure of the renormalization group, a number of problems [see (i)–(iv) below] may be solved simply and explicitly.

To do this, we first write down an appropriate differential equation based upon the Wegner-Houghton[7] differential generator for the renormalization group. Their functional integrodifferential equations may be simplified if we consider them in the limit of vanishing "external" momenta.[2] We find that for n-dimensional isotropically interacting spins $\vec{s}$ on a d-dimensional lattice, the renormalization action on the reduced Hamiltonian H is given by

$$\dot{H} = dH + (2-d)x\frac{\partial H}{\partial x} + \frac{d}{2}\left[1 - \frac{1}{n}\ln\left(1+\frac{\partial H}{\partial x}\right) + \frac{1}{n}\ln\left(1+\frac{\partial H}{\partial x} + 2x\frac{\partial^2 H}{\partial x^2}\right)\right], \tag{1}$$

where the dot denotes differentiation with respect to the renormalization parameter l, and $x \equiv (\vec{s} \circ \vec{s})/n$.[8] Since we have neglected the detailed momentum dependence in the renormalization group, we have set $\eta = 0$.

(i) *The general ϵ_Θ expansion.*—To solve (1), the Hamiltonian H can be expanded in terms of any complete set of functions; the expansion functions should be chosen to simplify the problem under consideration. A particularly useful set of functions are the eigenfunctions of (1) when (1) is linearized about