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PHOSPHORESCENCE MICROWAVE DOUBLE RESONANCE (PMDR) SPECTROSCOPY IN IONIC SOLIDS AND ITS APPLICATION TO COHERENT JAHN-TELLER STATES IN F CENTERS OF CaO

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PHOSPHORESCENCE MICROWAVE DOUBLE RESONANCE (PMDR)  
SPECTROSCOPY IN IONIC SOLIDS AND ITS APPLICATION TO  
COHERENT JAHN-TELLER STATES IN F CENTERS OF CaO.

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(Received May 1974)

We demonstrate the use of PMDR in ionic solids applied to the dynamic Jahn-Teller effect in F centers of CaO. The Jahn-Teller splitting ( $\Delta = 2.1 \text{ cm}^{-1}$ ) 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.

\* Alfred P. Sloan Fellow

† Work done in part under the auspices of the U. S. Atomic Energy Commission through the Inorganic Materials Research Division, Lawrence Berkeley Laboratory.

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Phosphorescence microwave double resonance spectroscopy (PMDR)<sup>1</sup> 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<sup>2,3</sup> which was subsequently extended to zero-field.<sup>4</sup> 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.<sup>5</sup>

Although many properties of ionic solids<sup>6</sup> are different from molecular solids, the basic features of excited F centers are similar to excited triplet states, particularly in zero-field. If one considers the F center oxygen vacancies in CaO, there is a one-to-one correlation of the individual spin sublevels of the F center in zero-field with  ${}^3B_{1u}$  molecular excited triplet states. In  $D_{4h}$ , the F center can be established<sup>7</sup> as a  ${}^3B_{1u}(\sigma, \sigma^*)$  state when the X axis of the zero-field tensor is defined along the  $C_4$  symmetry axis of the center. Many excited triplet states in molecular crystals have been unequivocally<sup>8</sup> 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<sup>9</sup> and spins<sup>10</sup> in molecular solids, and one might expect the same could be accomplished in ionic and semi-conducting 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 the Jahn-Teller<sup>11</sup> splittings from the zero-phonon origin in CaO, and finally, (c) determine a minimum coherence time for the Jahn-Teller split states and shed some light on how the coherence is lost, and its relationship to the dynamic Jahn-Teller effect.<sup>11</sup>

To illustrate the principles, we begin by summarizing the dynamic Jahn-Teller effect in cubic symmetry for triplet state F centers. Starting from a Hamiltonian describing two electrons in an oxygen vacancy having three equivalent axes (x, y, z), the Hamiltonian for two electrons correlated along any of the three axes, x(1 0 0), y(0 1 0) and z(0 0 1), where the indices (i, j, k) correspond to Miller indices associated with the CaO cubic structure, is simply:

$$H_{\text{total}} = \begin{bmatrix} H(1\ 0\ 0) & V(1\ 0\ 0, 0\ 1\ 0) & V(1\ 0\ 0, 0\ 0\ 1) \\ V(0\ 1\ 0, 1\ 0\ 0) & H(0\ 1\ 0) & V(0\ 1\ 0, 0\ 0\ 1) \\ V(0\ 0\ 1, 1\ 0\ 0) & V(0\ 0\ 1, 0\ 1\ 0) & H(0\ 0\ 1) \end{bmatrix}$$

Because of cubic symmetry, the vibronic matrix elements,  $V(i\ j\ k, i'\ j'\ k')$ , are all equal, and all  $H(i\ j\ k)$  elements are equal. The diagonal eigenfunctions of  $H_{\text{total}}$  are illustrated in Figure 1,

(hereafter called  $\psi(+ + +)$ ,  $\psi(+ - +)$  and  $\psi(- + -)$ ); and include the term,  $V(q, Q_1)$ , which is associated with Jahn-Teller induced nuclear displacement,  $Q_1$ . This gives rise to a splitting between  $\psi(+ + +)$  and  $\psi(\frac{+}{-} \frac{-}{+} \frac{+}{-})$  of  $\Lambda$ , sometimes referred to as the tunnel splitting. It is important to note that  $\psi(\ell m)$  are stationary solutions to the Schrödinger equation in the absence of a relaxation Hamiltonian; hence, the states  $\psi(\ell m)$  can be considered coherent in the absence of some relaxation. Additionally,

because the  $\psi(+ - +)$  and  $\psi(- + -)$  states involve linear combinations of the degenerate axes in the tetragonally distorted Jahn-Teller center, any off-diagonal matrix element in the diagonal basis of  $H_{\text{total}}$  will be equivalent for  $\psi(+ - +)$  and  $\psi(- + -)$  but different from  $\psi(+ + +)$ . Physically, we expect that the oscillator strength,  $f(\ell m)$ , resulting from spin-orbit coupling and responsible for phosphorescence from the  ${}^3\psi(+ - +)$  and  ${}^3\psi(- + -)$  states, will be the same in first order, but different from the  ${}^3\psi(+ + +)$  state. Additionally, we expect the spin-orbit contributions to the zero-field electron spin Hamiltonian for the dipolar splitting, which is off-diagonal, to be different for  ${}^3\psi(+ + +)$  than for the pair,  ${}^3\psi(+ - +)$  and  ${}^3\psi(- + -)$ ; hence, the zero-field splitting term,  $D$ , for the two electrons in the center will be different for  ${}^3\psi(+ + +)$  than for the  ${}^3\psi(+ - +)$  and  ${}^3\psi(- + -)$  states. Therefore, in first order the zero-field splitting is  $D(+ - +) = D(- + -) \neq D(+ + +)$ . Similar arguments have been applied to the zero-field splittings of coherent Frenkel exciton  $k$  states<sup>9</sup> and used to elucidate properties of coherent wavepackets.<sup>9</sup>

Coherence and the promoting mode<sup>11</sup> 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.<sup>12</sup>



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, Figure 1 diagrammatically illustrates the problem while Figure 2 (A-I) presents the experimental data on the F center in CaO. These include:  
the emission(2E)

and PMDR spectra in zero-field (2F; 2G) and 50 gauss (2H; 2I) at 1.5°K monitoring the zero-phonon<sup>13</sup> origin, (0,0), in addition to the ODMR results at 0 (2A), 10 (2B), 20 (2C), and 50 (2D) gauss.

CaO crystals were prepared by additive coloration<sup>14</sup> and had an F center concentration of  $5 \times 10^{17}$  centers/cc. CaO was excited with the 3100 Å region of a 100 watt high pressure Hg-Xe lamp. The zero-phonon<sup>13</sup> origin was isolated by a 1 meter spectrometer. Other experimental details are essentially the same as reported earlier<sup>8</sup> except that changes in microwave induced phosphorescence was phase detected at 105 cps.

The results from these experiments can be understood as follows: Two zero-field transitions, hereafter labeled  $\omega(+ + +)$  and  $\omega(\pm \mp \pm)$ , are seen at 1675.5 MHz and 1696.7 MHz respectively (cf. Figure (2A)). The PMDR spectrum of  $\omega(+ + +)$  (2F) 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  $\omega(\pm \mp \pm)$  (2G) yields two peaks symmetrically split from  $\omega(+ + +)$  by about  $4.2 \pm 0.2 \text{ cm}^{-1}$ . Moreover, the microwave induced change in phosphorescence increases for  $\omega(+ + +)$  and decreases for  $\omega(\pm \mp \pm)$  indicating the oscillator strengths  $f(+ + +) \neq f(\pm \mp \pm)$  and the populations of the stationary Jahn-Teller states are different. In the zero-field ODMR spectrum (2A) the splitting between the two components is 21 MHz and corresponds to  $2.1 \pm 0.1 \text{ cm}^{-1}$  in the unresolved optical spectrum. This means that the Jahn-Teller splitting or "tunnel splitting" is  $\Delta = 2.1 \pm 0.1 \text{ cm}^{-1}$ .

The fact that all three splittings are resolved in the PMDR spectrum (2F; 2G) means that the Jahn-Teller states are coherent in zero-field. A minimum coherence time can be established from exchange theory<sup>15</sup> which states

that intermediate exchange is given by the condition,  $[\omega(\pm \mp \pm) - \omega(+ + +)]\tau \sim$

1. The coherence time,  $\tau$ , in CaO is therefore longer than  $5 \times 10^{-8}$  seconds.

Thus, coherence persists in the Jahn-Teller states in zero-field at least  $6 \times 10^3$  times longer than that associated with the stochastic "random" incoherent limit, which is given by  $(2\Delta)^{-1}$  seconds. The coherence is associated with only one point in the full time correlation function,<sup>7</sup> namely  $5 \times 10^{-8}$  seconds.

From another point of view, if we assume that the linewidths at half height in the ODMR spectrum (2A), corresponding to  $\omega(+ + +)$ , 15.0 MHz, and  $\omega(\pm \mp \pm)$ , 10.7 MHz, are homogeneous, a minimum coherence time of  $7 \times 10^{-7}$  seconds for the  $^3\psi(+ + +)$  and  $1 \times 10^{-7}$  seconds for the  $^3\psi(+ - +)$  and  $^3\psi(- + -)$  can be obtained. In this case the coherence is persistent at least  $6 \times 10^2$  and  $4 \times 10^3$  times the stochastic limit for the  $^3\psi(+ + +)$  and  $^3\psi(\pm \mp \pm)$  states respectively at  $10^{-7}$  seconds in the time correlation function. Since CaO contains no nuclei that have nuclear spins, apart from  $^{43}\text{Ca}$  (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 linebroadening. This is not the case, since as one increases a D.C. H field, applied at approximately  $45^\circ$  to the (1 0 0) face, the ODMR spectra appear intermediately exchanged, not at zero-field, but at about 10 gauss (2B) and the microwave induced change in phosphorescence associated with  $\omega(+ + +)$  changes sign completely by 20 gauss (2C). This is simply because by 20 gauss the Jahn-Teller states are in an exchange limit on a time scale faster or comparable to the excited state lifetimes<sup>13</sup> ( $3 \times 10^{-3}$ ) of the  $^3\psi(\ell mn)$  states.

Because of the optical resolution of the PMDR spectrum in zero-field (2E; 2F), 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 gauss). The loss of coherence could also be decaying via some other channel, apart from scattering between the  $^3\psi(\ell m)$  states themselves. The loss of coherence via Zeeman terms, however, can be established. By 50 gauss the zero-field degenerate pair of spin sublevels,  $\omega'$  and  $\omega''$ , are clearly resolvable (2D). Furthermore, the system is in the fast exchange limit since the lines associated with  $\omega'(+ + +)$  and  $\omega'(\pm \mp \pm)$ , which are now mixed together by the Zeeman field, are narrower. Figure 2D shows that  $\omega'(+ + +)$  and  $\omega'(\pm \mp \pm)$  have linewidths at half heights of 8 MHz. Finally a PMDR on  $\omega'(+ + +)$  and  $\omega'(\pm \mp \pm)$  at 50 gauss (2H; 2I) 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  $10^{-3}$  seconds. This is established by the fact that the maximum in the PMDR (2H; 2I) and the maximum in the phosphorescence emission (2E) are coincident due to fast exchange relative to the F centers excited state lifetime ( $\sim 3 \times 10^{-3}$  seconds) 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  $^3\psi(+ + +)$ ,  $^3\psi(+ - +)$  and

$\psi(- + -)$  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.

### References

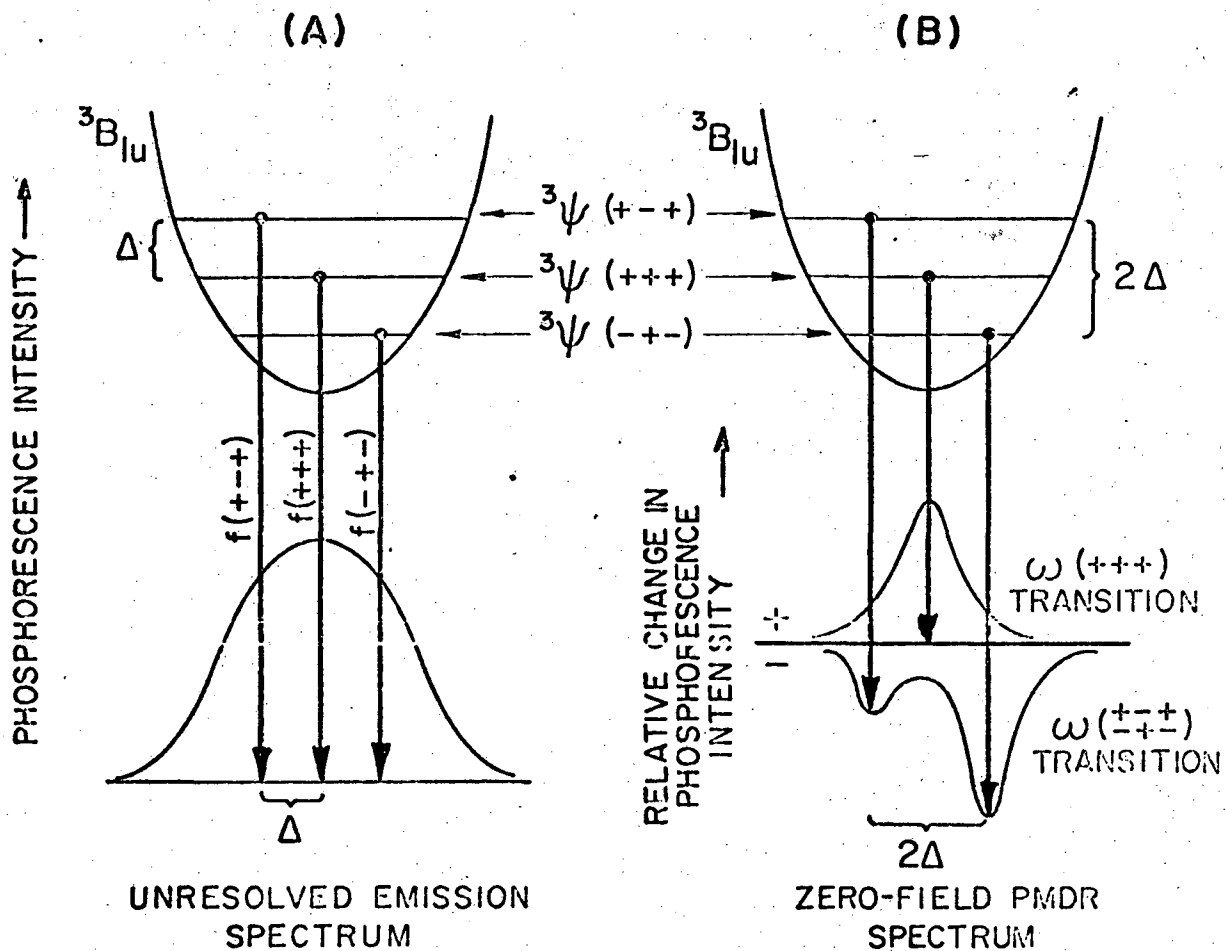
- <sup>1</sup>D. S. Tinti, M. A. El-Sayed, A. H. Maki and C. B. Harris, Chem. Phys. Lett. 3, 343 (1969).
- <sup>2</sup>M. S. Sharnoff, J. Chem. Phys. 46, 3263 (1967).
- <sup>3</sup>A. L. Kwiram, Chem. Phys. Lett. 1, 272 (1967).
- <sup>4</sup>J. Schmidt and J. H. van der Waals, Chem. Phys. Lett. 2, 640 (1968).
- <sup>5</sup>A. Kwiram, Optical Detection of Magnetic Resonance in Molecular Triplet States, M.T.P. International Rev. of Science, Physical Chem. Series 1, Vol. 4, pp. 271-316. Ed. C. A. McBowell, Butterworth Pub. Co., 1972.
- <sup>6</sup>Point Defects in Solids, Vol. 1: General and Ionic Crystals, J. H. Crawford, Jr., and L. M. Slifkin, ed., Plenum Press, New York (1972).
- <sup>7</sup>C. B. Harris, unpublished work.
- <sup>8</sup>A. H. Francis and C. B. Harris, J. Chem. Phys. 57, 1050 (1972).
- <sup>9</sup>A. H. Francis and C. B. Harris, Chem. Phys. Lett. 9, 181, 188 (1971).
- <sup>10</sup>C. B. Harris, R. L. Schlupp and H. Schuch, Phys. Rev. Lett. 30, 1019 (1973); W. G. Breiland, C. B. Harris and A. Pines, Phys. Rev. Lett. 30, 158 (1973).
- <sup>11</sup>H. A. Jahn and E. Teller, Proc. Roy. Soc. (London) A161, 220 (1937); F. S. Ham, Phys. Rev. 138, 1725 (1965).
- <sup>12</sup>P. Edel, C. Hennies, Y. Merle d'Aubigné, R. Romestain and Y. Twarowski, Phys. Rev. Lett. 28, 1268 (1972); P. Edel, Y. Merle d'Aubigné, and R. Louat, J. Phys. Chem. Solids 35, 67 (1974).
- <sup>13</sup>B. Henderson, S. E. Stokowski and T. C. Ensign, Phys. Rev. 183, 826 (1969).
- <sup>14</sup>E. B. Hensley, W. C. Ward, B. P. Johnson and R. L. Kroes, Phys. Rev. 175, 1227 (1968).
- <sup>15</sup>R. Kubo and K. Tomita, J. Phys. Soc. (Japan) 9, 888 (1954); P. W. Anderson, J. Phys. Soc. (Japan) 9, 316 (1954).

Figure Captions

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

Figure 2: ODMR results (2A-2D) and PMDR spectra (2B-2I) in F centers of CaO.

PMDR IN COHERENT JAHN-TELLER SPLIT F-CENTERS

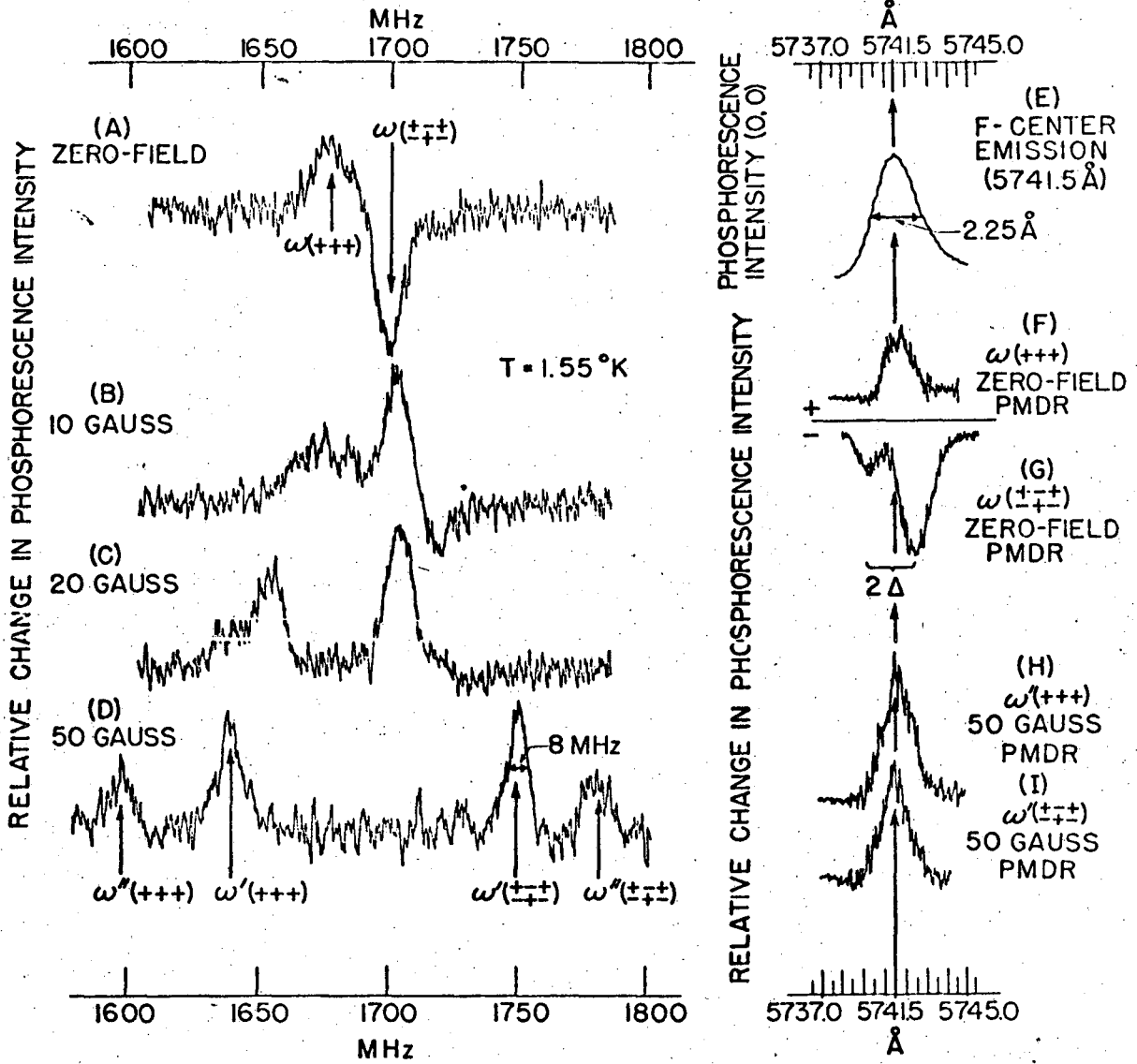


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Fig. 1

ODMR IN F-CENTERS OF CaO  
MONITORING THE (0,0) EMISSION

PMDR IN F-CENTERS OF CaO  
MONITORING THE (0,0) EMISSION



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Fig. 2



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