Dynamic Jahn-Teller effects in the photoluminescence of Fe^{2+} in $KMgF_3$

D. Walsh
Rutherford Physics Building, McGill University, Montreal, Quebec H3A 2T8

J. Lange
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74074

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The low-temperature zero-phonon lines and the corresponding phonon replica establish the energies of the $J=2$ and $J=3$ spin-orbit states to be 28 and 102 cm^{-1}, respectively, above the ground $J=1$ (Γ_{5g}) state. The Jahn-Teller coupling is to both T_{2g} and E_g modes, which are degenerate at a frequency corresponding to 288 cm^{-1}. These results help to clear up a long-standing controversy about the strength and type of Jahn-Teller coupling for the $^5T_{2g}$ state of this paramagnetic crystal.

The electronic states of Fe^{2+} in perfect octahedral coordination consist of a ground ^5D term, which is split by the cubic crystalline electric field into a $^5T_{2g}$ ground state and an excited ^5E_g state at approximately 10 000 cm^{-1} for Fe^{2+} substituting for Mg^{2+} in $KMgF_3$. Higher terms include ^3H and ^3P, and for the above crystalline electric fields one finds[1] that the lowest state is a $^3T_{1u}$ with energy approximately 14 500 cm^{-1}. The $^5T_{2g}$ state is split in first order by the spin-orbit coupling into a ground $J=1$ state above which lie the $J=2$ and $J=3$ spin-orbit states at 2λ and 5λ, respectively, where λ is the spin-orbit interaction ($\sim$100 cm^{-1}). Second-order spin-orbit corrections via the excited ^5E_g states remove some of the remaining degeneracy, the splitting of the $J=2$ states for the above crystal field being $\sim$6 cm^{-1}. The energy levels and corresponding irreducible representations are shown in Fig. 1, where the second-order corrections are neglected. The corresponding levels of the excited $^3T_{1u}$ are also included for later discussion. As Ham[2] first predicted, a strong dynamic Jahn-Teller coupling between the T_{2g} orbital state and the normal modes of the crystal may reduce considerably both the spin-orbit splitting and the g factor of the ground spin-orbit Γ_{5g} state. For instance, from the infrared absorption of Fe^{2+} in MgO by Wong[3] the Γ_{3g} and Γ_{4g} states of $J=2$ are considered to be degenerate at 105 cm^{-1} (absorption linewidth 9 cm^{-1}). In the strong-coupling limit the corresponding reduction in the orbital contribution to the g factor of the Γ_{5g} state would also be $\sim$50% giving $g=3.25$ which disagrees with the experimental value, $g=3.428$.[4] The discrepancy was removed by Ham *et al.*[5] by coupling to both E_g and T_{2g} modes in the weak Jahn-Teller coupling limit and adjusting the coupling to agree with the infrared results.

To date the experimental situation for Fe^{2+} in $KMgF_3$ is less clear. The strain coupling coefficients suggested a Jahn-Teller coupling considerably stronger than that in MgO,[5] although the g factor of the Γ_{5g} state was found to be 3.36 by Vallin and Piper[6] but 3.44 by Kim and Lange.[7] Frankel *et al.*[8] assigned the infrared absorption at 87 cm^{-1} to the Γ_{3g}, Γ_{4g} states of $J=2$, while Ray *et al.*[9] chose the main peak at 52 cm^{-1} for this assignment. More re-

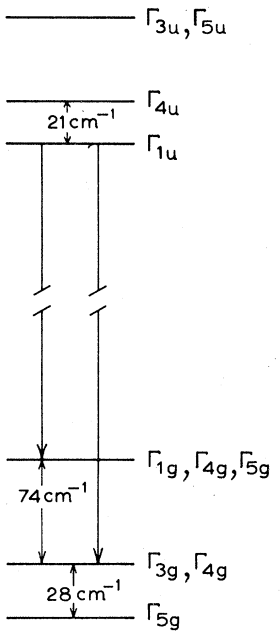

FIG. 1. Relative energy levels of the ground $^5T_{2g}$ and excited $^3T_{1u}$ states for Fe^{2+} in $KMgF_3$.

cently, Hjortsberg *et al.*[10] using both near infrared absorption at high temperatures and laser resonance in the far infrared in the presence of a magnetic field predicted the Γ_{3g}, Γ_{4g} states to be at ~ 30 cm^{-1}. In addition, there is considerable uncertainty about the type of Jahn-Teller coupling. From far infrared studies Ray *et al.*[9] prefer equal coupling to T_{2g} and E_g modes; the Mössbauer studies of Regnard *et al.*[11] indicate primarily T_{2g} coupling, while the acoustic relaxation data of Kim and Lange[12] was interpreted as evidence for coupling to T_{2g} modes only. The purpose of this report is to provide for the first time through photoluminescence accurate data on the following: the strength and type of Jahn-Teller coupling in the ground state, the frequency of the coupled normal modes, and the Jahn-Teller coupling strength in the excited $^3T_{1u}$ state.

Figures 2 and 3 show the photoluminescence of $KMgF_3$ doped with 0.4 at.% ferrous ion. The crystals were grown in the crystal growth facility, Oklahoma State University. The crystal, which had polished faces corresponding to the principal crystallographic directions, was immersed in liquid ^{4}He below the λ point in a Janis 8 DT optical Dewar. Excitation was by a Spectra Physics 171 krypton ion laser using 150 mW of focused light at 676.4 nm. A 90° scattering configuration was employed and the luminescence was spectrally analyzed with a Jobin Yvon HG 25 double monochromator using a cooled GaAs Hamamatsu R666S photomultiplier tube and standard photon-counting equipment. As is well known for similar paramagnetic crystals at 2 K, the optically excited ion thermalizes rapidly into the lowest excited state of the $^3T_{1u}$ manifold, i.e., Γ_{1u}. Weak spin-forbidden transitions are allowed only to the two Γ_{4g} ground states as shown in Fig. 1. These zero-phonon transitions can be seen in the luminescence of Figs. 2 and 3 at 14 239 and 14 165 cm^{-1}. Figure 2 shows also the phonon replicas of the 14 239 cm^{-1} line shifted by 288 cm^{-1}, which gives us the frequency of the Jahn-

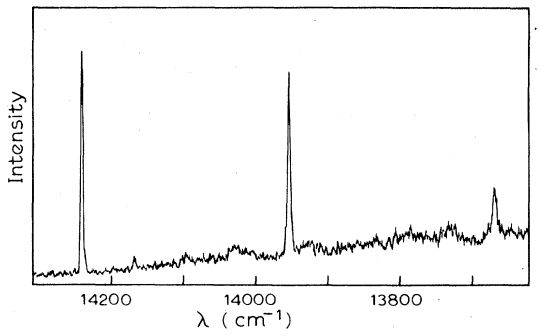

FIG. 2. Photoluminescence at 2 K of Fe^{2+} in $KMgF_3$ showing zero-phonon lines at 14 239 and 14 165 cm^{-1} and phonon replicas of the 14 239-cm^{-1} transition. Resolution ± 1 cm^{-1}, 150 mW at 676.4 nm.

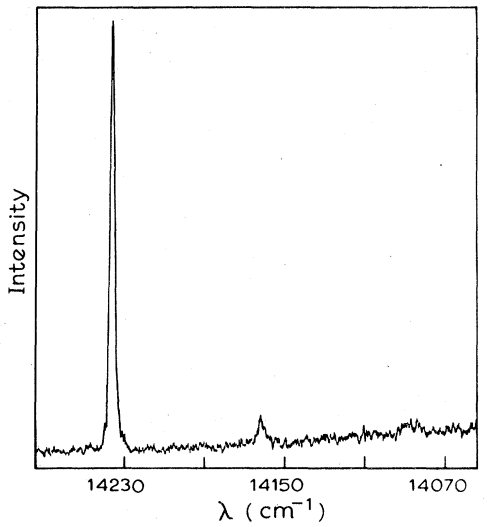

FIG. 3. Expanded scale of zero-phonon transitions in Fig. 2.

Teller coupled mode. At higher temperatures the Γ_{4u} level of the excited $^3T_{1u}$ manifold will be populated after laser excitation; consequently, other transitions will be allowed including that to the ground Γ_{5g} state. Figure 4 shows in addition to the low temperature zero-phonon luminescence two extra zero-phonon lines, one at 14 260 cm^{-1} corresponding to the transition $\Gamma_{4u} \rightarrow \Gamma_{3g}$, Γ_{4g}, and the other at 14 288 cm^{-1} corresponding to $\Gamma_{4u} \rightarrow \Gamma_{5g}$. The lower energy transition $\Gamma_{4u} \rightarrow \Gamma_{1g}$, Γ_{4g}, and Γ_{5g} corresponding to $J = 3$ does not appear above the background "hot" luminescence. Typical temperatures corresponding to Fig. 4 are approximately 5 K but due to absorption the crystal temperature is closer to 20 K. Greater laser heating effects occur when excitation is at 647.1 nm, but

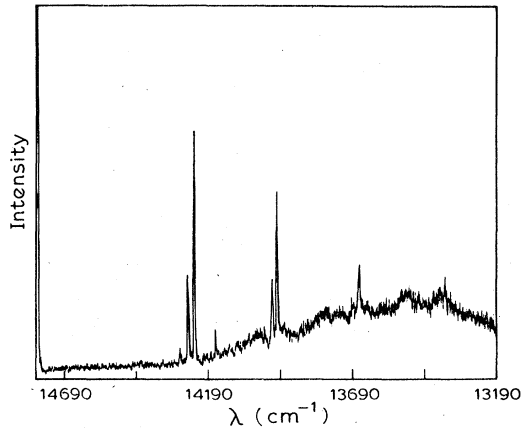

FIG. 4. Photoluminescence at approximately 20 K of Fe^{2+} in $KMgF_3$ showing zero-phonon transitions and phonon replicas. Conditions similar to that in Fig. 2.

otherwise the luminescence is identical. Figure 1 summarizes the energy level diagram using the data of Figs. 2, 3, and 4.

These results, which give approximately a Jahn-Teller energy four times that for Fe^{2+} in MgO, are consistent with our expectations, since the strain coupling coefficients of Fe^{2+} in $KMgF_3$ have been reported[13] to be twice that for ferrous doped MgO. The high-temperature zero-phonon line at 14 288 cm^{-1} was interpreted as the $\Gamma_{4u} \rightarrow \Gamma_{5g}$ transition and not the $\Gamma_{4u} \rightarrow \Gamma_{3g}$ transition which would imply a 28-cm^{-1} separation between Γ_{3g} and Γ_{4g} for the $J = 2$ states. The absence of a higher-frequency zero-phonon line to the ground Γ_{5g} is the justification for our choice of terminal state, although it must be pointed out that higher-energy emitted photons will be attenuated through absorption by phonon-assisted transitions to the excited term. On balance, our assignment with Γ_{3g} and Γ_{4g} degenerate is more acceptable; consequently, one must assume comparable couplings[5] to both the E_g and T_{2g} modes. (The energy levels of Fig. 1 are also consistent with the study of Hjortsberg *et al.*[10] which indicated that Γ_{3g} and Γ_{4g} are degenerate at approximately 30 cm^{-1}.) Furthermore, the phonon replicas imply that both modes are degenerate with a frequency corresponding to 288 cm^{-1}. This would be surprising for a Jahn-Teller continuum model but quite acceptable for a cluster model. Luminescence in the presence of uniaxial strain as well as electronic Raman spectroscopy is desirable and plans for such experiments are underway. However, there is sufficient evidence already to warrant a close reexamination of the ground state g factor of Fe^{2+} in $KMgF_3$ particularly if the experimental value of 3.44 is correct, since the corresponding experimental value for Fe^{2+} in MgO is 3.428. Finally, the 21-cm^{-1} separation between Γ_{4u} and Γ_{1u} (in the absence of Jahn-Teller coupling the separation is ~ 100 cm^{-1}) gives a measure of the strength of the Jahn-Teller coupling for the excited $^3T_{1u}$ manifold, the type of coupling for which will have to await luminescence studies in the presence of uniaxial strain.

[1]S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970), p. 110.
[2]F. S. Ham, Phys. Rev. 138, A1727 (1965).
[3]J. Y. Wong, Phys. Rev. 168, 337 (1968).
[4]D. H. McMahon, Phys. Rev. 134, A128 (1964).
[5]F. S. Ham, W. M. Scharz, and M. C. M. O'Brien, Phys. Rev. 185, 548 (1969).
[6]J. T. Vallin and W. W. Piper, Solid State Commun. 9, 823 (1971).
[7]H. Kim and J. Lange, Phys. Rev. Lett. 39, 501 (1977).
[8]R. Frankel, C. Abeledo, and A. Misetich, Solid State Commun. 12, 1147 (1973).
[9]T. Ray, J. Regnard, J. Laurent, and A. Ribeyron, Solid State Commun. 13, 1959 (1973).
[10]A. Hjortsberg, B. Nygren, and J. T. Vallin, Solid State Commun. 22, 619 (1977).
[11]J. Regnard, J. Chappert, and A. Ribeyron, Solid State Commun. 15, 1539 (1974).
[12]H. Kim and J. Lange, Phys. Rev. B 18, 1961 (1978).
[13]J. K. Wigmore, H. M. Rosenberg, and D. K. Garrod, J. Appl. Phys. 39, 682 (1968).