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Dynamic Jahn-Teller Effect in the $^4T_2$ Excited States of $d^{3,7}$ Ions in Cubic Crystals. I. V^{2+} in $KMgF_3$

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We have measured the spin-orbit splitting, Zeeman effect, and splitting under ⟨001⟩ stress of the lowest vibronic levels of the $^4T_2$ term of V^{2+} in the octahedral site of $KMgF_3$. The results are compared with the predictions of the Ham theory of the dynamic Jahn-Teller effect in the strong-coupling regime, extended to include the effects of interterm spin-orbit coupling. With essentially only one adjustable parameter, this comparison is a very searching test of the theory. Excellent quantitative agreement with the first-order theory is found. The second-order corrections are small, but are found to be in at least qualitative agreement with experiment.

1. INTRODUCTION

The Jahn-Teller effect is the instability of a complex which is in a degenerate electronic state against distortions which remove that degeneracy. In the static Jahn-Teller effect the complex remains distorted in a particular way long enough for the distortion to be detected experimentally. In the dynamic Jahn-Teller effect, the complex resonates between two or more equivalent modes of distortion, and the distortion is not directly observable.[1] It was pointed out by Ham[2] (though special cases had been noted earlier[3]) that, in spite of this, profound changes in such observables as spin-orbit splittings, trigonal field splittings, and g factors in orbital triplet states can occur as a result of the dynamic Jahn-Teller effect. These changes are collectively known as the Ham effect.

The observable consequences of the Ham effect in the optical spectra of transition-metal ions have been explored in a number of papers.[4–7] It so happens that none of the systems studied were ideal for illustrating the effects predicted. In particular, the best data have been obtained on $3d$ ions substituted for Al^{3+} in α-Al_2O_3. This crystal has many desirable properties from an experimentalist's point of view, but it suffers from the grave disadvantage that the octahedron of O^{2-} ions surrounding the Al^{3+} ion is greatly distorted. It has been pointed out by Stephens[8] that this trigonal distortion is too large to be treated as a small perturbation on a system with cubic symmetry, as was done in the first applications of Ham's theory.[4,6,7] Stephens' treatment, which includes the trigonal distortion in a more accurate manner, necessarily introduces extra parameters which cannot be checked independently.

The data of Slack, Ham, and Chrenko[5] on tetrahedrally coordinated Fe^{2+} were obtained with cubic crystals. However, the data are too sparse to provide more than a qualitative check on the Ham theory.

In cubic crystals subject to uniaxial stress there can be no doubt as to the correctness of treating the effect of strain on the electronic energy levels as a small perturbation. Furthermore, for ions of the $3d$ series the spin-orbit coupling is usually weak relative to the Jahn-Teller interactions. We have studied the following octahedrally coordinated impurity systems: V^{2+}, Ni^{2+}, and Co^{2+} substituted for Mg^{2+} in MgO; and V^{2+} and Co^{2+} substituted for Mg^{2+} in $KMgF_3$. In each case the ground state is too weakly coupled to the lattice to be subject to an appreciable Jahn-Teller effect. Transitions from this state to the lowest spin-allowed excited state ($^4T_2$ for V^{2+} and Co^{2+}, $^3T_2$ for Ni^{2+}) show sharp-line structure at the band origin (no-phonon lines).[9–11] This structure arises from the spin-orbit coupling, and further splittings can be produced by uniaxial stress, or by a magnetic field. In many cases the matrix elements of strain, spin-orbit coupling, and orbital momentum can be determined from independent data, so that the only adjustable parameters are those describing the Jahn-Teller interaction.

The results on MgO:V^{2+} have already been reported.[10] It was found that the Ham theory with coupling only to E_g vibrations is unable to account for the data, which still remain something of a mystery.[12] Stress and Zeeman data on MgO:Ni^{2+} have been reported briefly elsewhere.[13] The data showed some indications of a Ham effect, but were insufficient for a quantitative comparison with theory. Work on Co^{2+} is reported

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[1] For a discussion of the observable consequences of the Jahn-Teller effect, and a review of the experimental situation up to mid-1967, see M. D. Sturge, in *Advances in Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press Inc., New York, 1967), Vol. 20, p. 91.

[2] F. S. Ham, Phys. Rev. **138**, A1727 (1965).

[3] H. M. McConnell, J. Chem. Phys. **34**, 13 (1961).

[4] W. C. Scott and M. D. Sturge, Phys. Rev. **146**, 262 (1966).

[5] G. A. Slack, F. S. Ham, and R. M. Chrenko, Phys. Rev. **152**, 376 (1966).

[6] R. M. Macfarlane, J. Y. Wong, and M. D. Sturge, Phys. Rev. **166**, 250 (1968).

[7] P. J. Stephens and M. Lowe-Pariseau, Phys. Rev. **171**, 322 (1968).

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[9] R. Pappalardo, D. L. Wood, and R. C. Linares, Jr., J. Chem. Phys. **35**, 1460 (1961); **35**, 2041 (1961).

[10] M. D. Sturge, Phys. Rev. **140**, A880 (1965).

[11] R. E. Dietz, L. F. Johnson, and H. J. Guggenheim (unpublished).

[12] F. S. Ham, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (John Wiley & Sons, Inc., New York, 1967), p. 357.

[13] M. D. Sturge and K. A. Ingersoll, Bull. Am. Phys. Soc. **12**, 60 (1967).

separately. Discrepancies are found in this case which indicate the need for a more elaborate theory.

Here we report our results on $KMgF_3{:}V^{2+}$. Interterm spin-orbit coupling turns out to be very important in this system. We take it into account by setting up an effective Hamiltonian for the $^4T_2$ term in which the parameters are determined by a crystal-field calculation, not by fitting to experiment. The only adjustable parameter of any significance in the fitting of theory to experiment is x, the first-order Jahn-Teller coupling parameter. With this single parameter we find we can fit a wealth of experimental data, and perform a very thorough test of the theory.

2. THEORY

The Hamiltonian for a transition-metal ion of the d^n configuration, placed in a cubic crystal field and subject to an external perturbation (stress or magnetic field), can be written

$$\mathcal{H}=\mathcal{H}_{\mathrm{FI}}+\mathcal{H}_{\mathrm{cub}}+\mathcal{H}_{ls}+\mathcal{H}_{\mathrm{pert}}+\mathcal{H}_{\mathrm{JT}}. \tag{1}$$

The first four terms are purely electronic. They represent, respectively, the interelectronic repulsion which leads to term separations in the free ion ($\sim 10^4$ cm^{-1}); the cubic crystal field ($\sim 10^4$ cm^{-1}); the spin-orbit coupling (10^2 to 10^3 cm^{-1}); and the external perturbation (~ 10 cm^{-1}). The last term $\mathcal{H}_{\mathrm{JT}}$ ($\sim 10^2$ to 10^3 cm^{-1}) represents the lattice vibrations and their Jahn-Teller interaction with the d electrons (non-Jahn-Teller interactions, such as those with totally symmetric modes of vibration, are of no direct interest and are ignored). For the d^n configuration with n not equal to 1 or 9, the exact solution of (1) is impracticable even for the simplest possible $\mathcal{H}_{\mathrm{JT}}$, and we divide up the problem as follows.

The solution of the cubic-field problem ($\mathcal{H}_{\mathrm{FI}}+\mathcal{H}_{\mathrm{cub}}$) for any d^n system has been given by Tanabe and Sugano.[14] The free-ion terms are split and mixed to give a new set of "cubic terms" characterized by their spin S (or multiplicity, $2S+1$) and by the transformation properties of their orbital wave functions under the operations of the cubic group. We are interested in those cubic terms which are (orbitally) triply degenerate: They are labeled $^{2S+1}T_1$ or $^{2S+1}T_2$.

In a rigid cubic lattice ($\mathcal{H}_{\mathrm{JT}}=0$, $\mathcal{H}_{\mathrm{pert}}=0$) these terms are further split by the spin-orbit interaction $\mathcal{H}_{ls}$. The complete matrices of $\mathcal{H}_{\mathrm{FI}}+\mathcal{H}_{\mathrm{cub}}+\mathcal{H}_{ls}$ have been calculated for the $d^{3,7}$ configuration by Eisenstein.[15] With a large computer it is a relatively simple matter to diagonalize these matrices and to obtain the energy levels the ion would have in a rigid lattice. (The choice of parameters in such a calculation is discussed later.) We find that, although the calculated spin-orbit splitting of a cubic term is usually small relative to its separation from other terms, the contributions of off-diagonal elements of $\mathcal{H}_{ls}$ (i.e., those connecting different cubic terms) are often very important. We can describe the spin-orbit splittings of a cubic term by an effective Hamiltonian of second order in L and S, whose form is dictated by the cubic symmetry[5,16]:

$$\mathcal{H}_{\mathrm{eff}}=-\lambda\mathbf{L}\cdot\mathbf{S}+\kappa(\mathbf{L}\cdot\mathbf{S})^2 +\rho(L_x^2S_x^2+L_y^2S_y^2+L_z^2S_z^2). \tag{2}$$

Here $\mathbf{S}$ is the spin and $\mathbf{L}$ is the effective orbital-momentum operator within the cubic term ($L=1$ for a T_1 or T_2 term). The parameters λ, ρ, and κ are fitted to the calculated energy levels. Since $\mathcal{H}_{ls}$ is linear in $\mathbf{S}$ (no Trees term[17] being included), the terms in κ and ρ arise solely from off-diagonal elements of $\mathcal{H}_{ls}$.

We now apply the Jahn-Teller interaction $\mathcal{H}_{\mathrm{JT}}$ to the cubic term, leaving $\mathcal{H}_{\mathrm{eff}}$ to be treated as a perturbation. At first sight it may seem illogical to neglect off-diagonal elements of $\mathcal{H}_{\mathrm{JT}}$, when we have included those of $\mathcal{H}_{ls}$. However, in the cases we later discuss, we are interested only in terms of maximum multiplicity (spin quartets) and these are well separated from each other. Since $\mathcal{H}_{\mathrm{JT}}$ is spin-independent, it only connects terms of the same multiplicity. On the other hand, $\mathcal{H}_{ls}$ connects terms of different multiplicity, and these tend to approach each other closely: For instance, in $KMgF_3{:}V^{2+}$, ^2E and $^2T_1$ are both within 1000 cm^{-1} of the $^4T_2$ term of interest. It is primarily interaction with these states of lower multiplicity which give rise to the large κ and ρ terms in Eq. (2). Furthermore, whereas the off-diagonal terms of $\mathcal{H}_{ls}$ produce qualitative and easily observable changes in the energy-level spectra, the off-diagonal elements of $\mathcal{H}_{\mathrm{JT}}$ do nothing but alter parameters which are rather uncertain anyway. This point is discussed further below.

The problem of the Jahn-Teller interaction of a triply degenerate cubic term with vibrations of E_g or T_{2g} symmetry has been treated very thoroughly by Ham.[2] Here we summarize his treatment. We assume that interaction with the T_{2g} vibrations can be neglected. This assumption, which enormously simplifies the problem, can only be justified in each individual case by the final comparison with experiment. It is *a priori* reasonable that the E_g mode of an octahedron, which involves radial motion of the ligand ions and can couple to σ-bonding orbitals, should couple more strongly than the T_{2g} mode, which only involves tangential motion and couples only to π-bonding orbitals. We follow Ham in assuming that the continuum of vibrational modes with E_g character can be approximated by a single mode with an effective frequency ω, mass μ, and coupling constant V.

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[14] Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954); **9**, 766 (1954).

[15] J. C. Eisenstein, J. Chem. Phys. **34**, 1628 (1961).

[16] J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 177 (1957).

[17] R. E. Trees, Phys. Rev. **82**, 683 (1951).

The collective coordinates of the E_g mode are conventionally known as $Q_2(\sim x^2-y^2)$ and $Q_3(\sim 3z^2-r^2)$. The Jahn-Teller term in the effective Hamiltonian for a triplet is[18]

$$\mathcal{H}_{JT}=\frac{1}{2\mu}\sum_{k=2,3}(-\hbar^2\partial^2/\partial Q_k^2+\mu^2\omega^2Q_k^2)-V\begin{bmatrix}-\frac{1}{2}Q_3+(\sqrt{\frac{3}{2}})Q_2 & 0 & 0\\ 0 & -\frac{1}{2}Q_3-(\sqrt{\frac{3}{2}})Q_2 & 0\\ 0 & 0 & Q_3\end{bmatrix}. \quad (3)$$

This acts on the state vector $[a,b,c]$ where the electronic wavefunction is $a|\xi\rangle+b|\eta\rangle+c|\zeta\rangle$, (ξ,η,ζ) describing a real basis for the orbital triplet.

We direct our attention to the lowest vibronic level. This is triply degenerate and transforms in the same way as the electronic parent (the "bare cubic term," whose energy is taken as zero). Its energy is $-E_{\mathrm{JT}}$ where $E_{\mathrm{JT}}=V^2/2\mu\omega^2$. If $\mathcal{H}_{\mathrm{eff}}\lesssim E_{\mathrm{JT}}$, we can use perturbation theory. To first order in $\mathcal{H}_{\mathrm{eff}}$, matrix elements within the level are given by

$$\langle Mi00|\mathcal{H}_{\mathrm{eff}}^{\mathrm{I}}|M'j00\rangle =[\delta_{ij}+\gamma(1-\delta_{ij})]\langle Mi|\mathcal{H}_{\mathrm{eff}}|M'j\rangle, \quad (4)$$

where $\gamma=e^{-x/2}$, and x is the basic Jahn-Teller parameter $3E_{\mathrm{JT}}/\hbar\omega$. M and M' are spin magnetic quantum numbers, and i, $j=\xi,\eta,\zeta$.

In second order, we have

$$\langle Mi00|\mathcal{H}_{\mathrm{eff}}^{\mathrm{II}}|M'j00\rangle=-[f_b\delta_{ij}+(1-\delta_{ij})f_a]/\hbar\omega \times\sum_{k,M''\ (k\neq i,j)}\langle Mi|\mathcal{H}_{\mathrm{eff}}|M''k\rangle\langle M''k|\mathcal{H}_{\mathrm{eff}}|M'j\rangle. \quad (5)$$

The quantities γ, f_a, and f_b are functions only of x. They are tabulated by Ham[2] and plotted in Fig. 5 of Ref. 6. Note that, whereas in first order the Jahn-Teller interaction is described by one parameter, x, in second order $\hbar\omega$ appears explicitly.

This calculation has been extended numerically to higher orders by Ham and Schwartz.[19] They find that in the case of the d^1 system Al_2O_3:Ti^{3+}, the first two terms give quite a good approximation even when the second-order terms are as large as the first (in this case the principal contribution to $\mathcal{H}_{\mathrm{eff}}$ is not the spin-orbit coupling but the trigonal crystal field). In the present work, we find the second-order terms to be relatively small for any reasonable value of $\hbar\omega$, and good convergence should not be in doubt.

We treat $\mathcal{H}_{\mathrm{pert}}$, the external perturbation, in just the same way as $\mathcal{H}_{\mathrm{eff}}$, except that second-order terms are now completely negligible. For $\langle 001\rangle$ stress, we have

$$\langle Mi00|\mathcal{H}_{001}|M'j00\rangle=-\delta_{ij}\delta_{MM'}u(L_z^2-\tfrac{2}{3}), \quad (6)$$

where u is the tetragonal splitting of the bare orbital triplet under the applied stress. Since $\mathcal{H}_{001}$ is diagonal in the (ξ,η,ζ) representation, the splitting is the same as in the absence of the Jahn-Teller effect. Deviations from the expected splitting can only arise from Jahn-Teller-induced mixing of the electronic terms. In $KMgF_3$:V^{2+}, where we can determine u from independent measurements on the ground term, we find this effect to be quite small (see below).

A $\langle 111\rangle$ stress has only off-diagonal elements in this representation:

$$\langle Mi|\mathcal{H}_{111}|M'j\rangle=-\tfrac{1}{3}\delta_{MM'}(1-\delta_{ij})\gamma v, \quad (7)$$

where v is the trigonal splitting of the bare term. Thus the trigonal splitting is reduced by the Ham factor γ. Unfortunately we have usually no reliable independent value of v (though we can estimate it from the point-charge model in some cases) and this relation can only be checked qualitatively.

Finally, we can apply a magnetic field along either an $\langle 001\rangle$ or a $\langle 111\rangle$ direction. To obtain the perturbation matrix to first order in the Zeeman interaction, and to second order in $\mathcal{H}_{\mathrm{eff}}$, we calculate the full first- and second-order matrix of $\mathcal{H}_{\mathrm{eff}}$ in the real basis and then rotate to a complex basis quantized along **H**. For $H\|\langle 001\rangle$ field, the rotation matrix operates only on the orbital part and is simply

$$\begin{bmatrix}2^{-1/2} & 2^{-1/2}i & 0\\ 2^{-1/2} & -2^{-1/2}i & 0\\ 0 & 0 & 1\end{bmatrix}.$$

For $H\|\langle 111\rangle$ we have to rotate both spin and orbital parts. The rotation matrix from $\langle 001\rangle$ to $\langle 111\rangle$ is the direct product

$$\mathfrak{D}^{(L)}(\pi/4,\beta,0)\times\mathfrak{D}^{(S)}(\pi/4,\beta,0)$$

(where $\beta=\cos^{-1}3^{-1/2}$, $L=1$, $S=\frac{3}{2}$), and can be calculated by the method given by Edmonds.[20]

To the matrix of $\mathcal{H}_{\mathrm{eff}}$, now in a complex basis quantized along **H**, we simply add the matrix elements of the Zeeman operator, which is diagonal in this basis. To first order, we have

$$\mathcal{H}_z^{\mathrm{I}}=\beta H(\gamma KL_z+2S_z),$$

where $K=\langle 1|L_z|1\rangle$ for the "bare" cubic term. For ${}^4T_2$ of d^3, $K=-\frac{1}{2}k$, while for d^7, $K=+\frac{1}{2}k$, where k is the orbital reduction factor for a single t_2 electron.[21] Because **L** is off-diagonal in the original, real basis, the orbital

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[18] U. Öpik and M. H. L. Pryce, Proc. Roy. Soc. (London) **A238**, 425 (1957).

[19] F. S. Ham and W. M. Schwartz (unpublished).

[20] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, (Princeton University Press, Princeton, N. J., 1957).

[21] S. Sugano and M. Peter, Phys. Rev. **122**, 381 (1961).

contribution to the Zeeman splitting is reduced by the factor γ, and the choice of k (approximately 0.9 in $KMgF_3:V^{2+}$ [22]) is not critical. The primary purpose of a Zeeman measurement is to check the correctness of the spin wave functions calculated by the Ham theory. Deviations from the theory can occur because of mixing of terms of different multiplicity by $\mathcal{H}_{ls}$. Inspection of the wave functions obtained in the crystal-field calculation shows that this should be a small effect in the cases of interest.

To sum up, we have extended the Ham theory to the case of a cubic term interacting with neighboring terms, by replacing $\mathcal{H}_{ls}$ with $\mathcal{H}_{\mathrm{eff}}$. This replacement takes into account, in an approximate but adequate manner, the mixing of terms by the spin-orbit interaction. Our method should work so long as mixing of terms by the Jahn-Teller interaction is not too strong, and if interaction with T_{2g} vibrations can be neglected. We can determine the Jahn-Teller parameter x (and, if second-order effects are important, an effective value of $\hbar\omega$) by comparison of the theory with the observed spin-orbit splittings of the lowest vibronic level. Stress splittings can then be calculated with one further parameter (u or v) which may be determinable from other data. The Zeeman pattern can be calculated without additional parameters.

3. EXPERIMENTAL

Most of the measurements were made with a Cary 14RI double-beam spectrophotometer, with three major modifications:

(1) We substituted a dry-ice-cooled RCA 7102 photomultiplier for the uncooled detector supplied by the manufacturers.

(2) For the stress measurements, where small samples (roughly 2 mm square by 5 mm long) are required, we used a lens system in the specimen chamber to reduce the slit size by a factor of 3.

(3) Zeeman measurements were made with a 70-kG superconducting solenoid.

The resolution of the Cary 14RI under the conditions of these experiments was approximately 1.5 cm^{-1}. We checked some of the sharper features of the spectra on a single-beam Jarrell-Ash 1.8-m Ebert-Fastie spectrometer with a resolution of 0.1 cm^{-1}. No new structure was resolved, and because the absorption in the available samples was typically only a few percent, we preferred the double-beam instrument.

The only $KMgF_3:V^{2+}$ available was a polycrystalline boule containing 3×10^{19} (V^{2+} ions)/cm^3 used in a more general study of this system to be described in a forthcoming paper.[22] It was possible to cut from this a sample a few millimeters on the side in which the crystal axes did not wander more than a few degrees from the nominal direction. For $\langle 001\rangle$ (nominal) stress measurements, and for the Zeeman work, this alignment was good enough. It was not good enough for $\langle 111\rangle$ stress measurements, since an average deviation of (say) 5° from $\langle 111\rangle$ is enough to produce a tetragonal splitting of the lines which completely swamps the true trigonal splitting (if any).

4. COMPARISON OF EXPERIMENT WITH THEORY

The crystal-field parameters for V^{2+} in $KMgF_3$ can be obtained from the broad band absorption and emission spectra, which is reported in a forthcoming paper.[22] The spin-orbit coupling parameter ζ is obtained from the ground-state g factor. Since we are interested in the lowest vibrational levels of $^4T_2$, the appropriate parameters are those obtained in emission. We find $\Delta=10\,000$ cm^{-1}, $B=720$ cm^{-1}, $C=2520$ cm^{-1}, and $\zeta=150$ cm^{-1}; the latter three parameters are unlikely to be much affected by lattice relaxation in the $^4T_2$ state. Of these four parameters, only the uncertainty in ζ ($\pm7\%$) is at all troublesome.

The spin-orbit splitting of $^4T_2$ calculated from Eisenstein's matrices[15] for the static crystal-field problem, with the above values of the parameters, is shown at the left-hand side of Fig. 1. These splittings can be fitted within 1% by $\mathcal{H}_{\mathrm{eff}}$ [Eq. (2)] with the following parameters: $\lambda=-22$ cm^{-1}, $\kappa=2.5$ cm^{-1}, $\rho=-9$ cm^{-1}. The second-order contributions, which arise mostly from interactions with the ^2E and $^2T_1$ terms, are quite substantial. Note that $\mathcal{H}_{\mathrm{eff}}$ is merely a convenient description of the spin-orbit splittings calculated

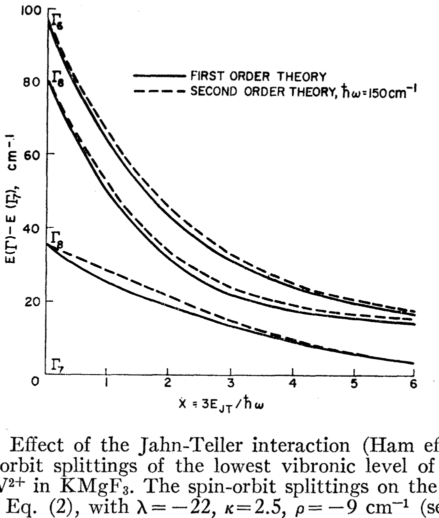

FIG. 1. Effect of the Jahn-Teller interaction (Ham effect) on the spin-orbit splittings of the lowest vibronic level of the $^4T_2$ term of V^{2+} in $KMgF_3$. The spin-orbit splittings on the left are given by Eq. (2), with $\lambda=-22$, $\kappa=2.5$, $\rho=-9$ cm^{-1} (see text). The effect of including second-order Ham effect terms, as indicated by the dashed lines, is seen to be extremely small. Note also the interaction between the two Γ_8 levels, which arises from the κ and ρ terms in Eq. (2). The limiting splitting for $x\gg1$ is $-2(\kappa+\rho)=+13$ cm^{-1}.

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[22] M. D. Sturge, F. R. Merritt, L. F. Johnson, J. P. van der Ziel, and H. J. Guggenheim (to be published).

neglecting the Jahn-Teller effect. The parameters λ, κ, and ρ are functions of Δ, B, C, and ζ.

The Ham effect [Eq. (4)] reduces these splittings as shown in Fig. 1. We can fit the three observed splittings (within ±10%) equally well with or without the second-order terms [Eq. (5)], which only contribute shifts of order 2 cm^{-1}.[23] Hence we cannot derive a value of $\hbar\omega$ from the data. The lowest value of $\hbar\omega$ consistent with the vibronic spectrum is 150 cm^{-1}; this should give an upper limit to the second-order contribution. With this value of $\hbar\omega$ we get the best fit with $x=2.6$ as shown in Fig. 2. The corresponding Ham quenching factor γ $(=e^{-x/2})$ is 0.27, and $E_{\mathrm{JT}}/\lambda \gtrsim 6$, so that our perturbation expansion should be convergent.

Once the Jahn-Teller parameters are known the Zeeman effect is completely determined. (Reasonable variations of the orbital reduction factor k about its most probable value of 0.9 do not appreciably affect the results.) With 48 possible transitions between ${}^4A_2$ and ${}^4T_2$, and a pronounced Paschen-Back effect, it is not a trivial matter to find the Zeeman splittings of the upper levels from the experimental data. We determined the initial state of each observed transition from the temperature dependence of its intensity (assuming a Boltzmann distribution over the ground quartet). The symmetry of the final state was then found from the polarization and the magnetic-dipole selection rules given in Table I (the symmetry is C_{4h} for $H\|\langle 001\rangle$ and C_{3i} for $H\|\langle 111\rangle$).[24] Assignments were checked by a detailed comparison of observed and calculated intensities as a function of temperature. Typical such comparisons are shown in Figs. 3 and 4.[25] Apart from a certain amount of depolarization in the axial (α) spectra (attributable to the finite aperture and to crystal imperfection), agreement is excellent.

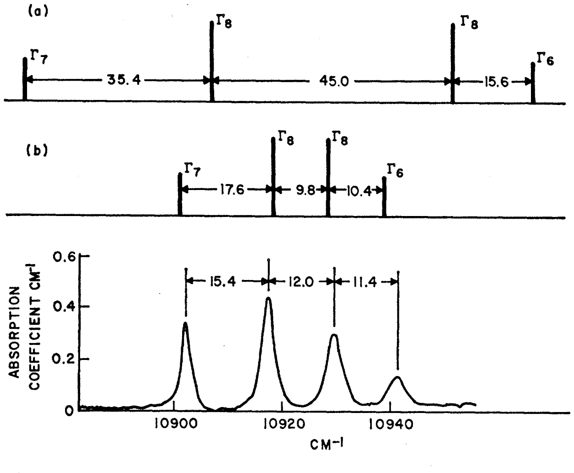
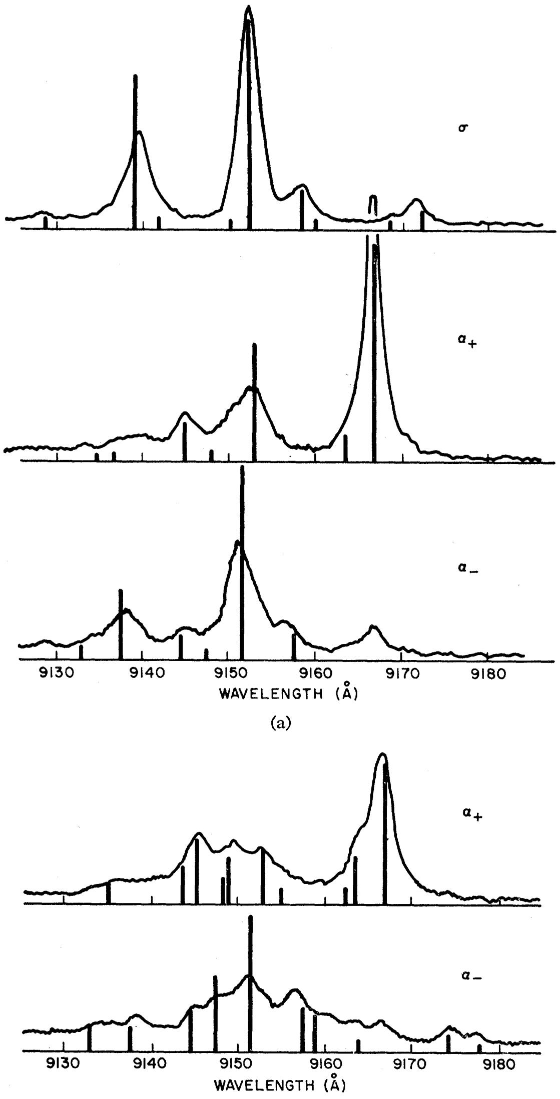


FIG. 2. Spin-orbit splittings of the lowest vibronic level of the ${}^4T_2$ terms in $\mathrm{KMgF_3{:}V^{2+}}$. (a) Splittings in cm^{-1} calculated from static crystal-field theory, using the parameters of Ref. 22. The predicted relative intensity of transitions from the ${}^4A_2$ ground term is indicated by the height of the sticks. (b) Splittings as reduced by the Ham effect: $x=2.6$, $\hbar\omega=150$ cm^{-1}. (c) Observed zero-field spectrum of $\mathrm{KMgF_3{:}V^{2+}}$ at 2°K.



(a)

(b)

FIG. 3. Zeeman spectra of $\mathrm{KMgF_3{:}V^{2+}}$ with $H=70$ kG parallel to $\langle 001\rangle$, compared with the calculation including the Jahn-Teller effect. (a) $T=5°\mathrm{K}$; (b) $T=20°\mathrm{K}$.

The positions and symmetries of the excited states are compared with theory in Figs. 5 and 6.[25] For the Γ_7 and Γ_6 doublet levels, g factors can be obtained from the data; we find $g=3.01\pm0.07$ for Γ_7 and 1.76 ± 0.10

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[23] While second-order effects could well be ignored altogether as far as the spin-orbit splitting and Zeeman effect are concerned, we find that their inclusion improves the fit to the stress data.

[24] We use Γ_i to label irreducible representations of the O_h group, while $\hat{\Gamma}_i$ refers to an axial group (C_{4h} or C_{3i}).

[25] In Figs. 2–6, we have displaced the theoretical Zeeman pattern for each level so as to agree with the experimental position in zero field. This can lead to appreciable errors in the Paschen-Back effect only when states of the same symmetry, originating from different levels, approach closely: for instance the $\hat{\Gamma}_7$ states near 10 927 cm^{-1} in Fig. 5.

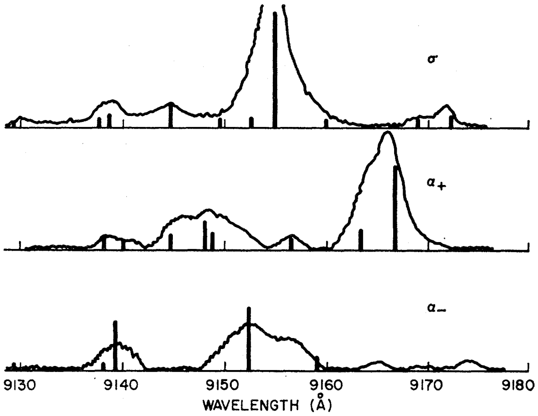

FIG. 4. Same as Fig. 3, but with H parallel to ⟨111⟩ and $T=10°$K.

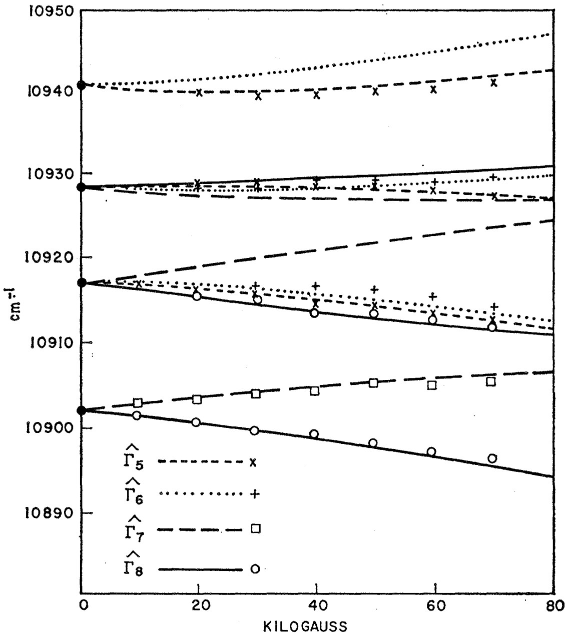

FIG. 5. Splitting of the ${}^4T_2$ term of KMgF$_3$:V^{2+} by a magnetic field parallel to ⟨001⟩. States are labeled by their symmetries in C_{4h}. Lines: theory. Points: experiment.

for Γ_6. These are to be compared with theoretical values of 3.414 and 1.90, respectively. Because of the Paschen-Back effect, some discrepancy between effective g factors for $H\sim 70$ kG and calculated g factors for $H\rightarrow 0$ is to be expected; however, the 12% discrepancy observed for Γ_7 is too large to be accounted for in this way. It is probable that the ${}^4T_2$ term is not quite such a pure spin quartet as we have assumed.

Apart from this relatively small discrepancy, over-all agreement between experiment and theory is excellent. That this is a significant test of the Ham theory can be seen as follows. We take $\mathcal{H}_{\mathrm{eff}}$ alone, and after arbitrarily adjusting λ, κ, and ρ to fit the observed zero-field splittings, calculate the Zeeman pattern as if there were no Jahn-Teller effect at all. Some spectra calculated in this way are compared with experiment in Figs. 7 and 8. The fit is substantially worse.

Because the matrix elements of $\mathbf{L}$ within the ${}^4T_2$ term are anyway small,[21] and are further reduced by the Ham quenching factor $e^{-x/2}$, the orbital contribution to the Zeeman splitting is too small to matter. Thus the fit obtained here is a test primarily of the accuracy of our spin-wave functions (except insofar as the transition probabilities are determined by the orbital-wave functions).

The orbital wave functions are tested by measuring the behavior of the spectrum under ⟨001⟩ stress. The

TABLE I. Magnetic dipole selection rules for the Zeeman effect. σ: H vector of light parallel to static field; α_+: right-hand circular polarization; α_-: left-hand circular polarization; F: forbidden

(a) C_{4h} symmetry: $\mathbf{H}\|\langle 001\rangle$

Initial state	M_s [a]	Final state Γ_5	Γ_6	Γ_7	Γ_8
Γ_5	$-\frac{3}{2}$	σ	α_-	F	α_+
Γ_6	$+\frac{3}{2}$	α_+	σ	α_-	F
Γ_7	$+\frac{1}{2}$	F	α_+	σ	α_-
Γ_8	$-\frac{1}{2}$	α_-	F	α_+	σ

(b) C_{3i} symmetry: $\mathbf{H}\|\langle 111\rangle$

Initial state	M_s [a]	Final state Γ_4	Γ_5	Γ_6
Γ_4	$+\frac{1}{2}$	σ	α_-	α_+
Γ_5	$-\frac{1}{2}$	α_+	σ	α_-
Γ_6	$\pm\frac{3}{2}$	α_-	α_+	σ

[a] Spin substate of the ${}^4A_2$ ground term.

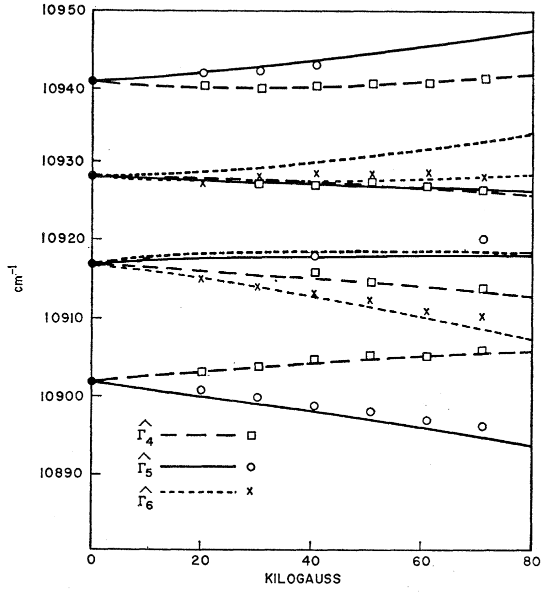

FIG. 6. Same as Fig. 5 with the magnetic field parallel to ⟨111⟩. States are labeled by their symmetries in C_{3i}.

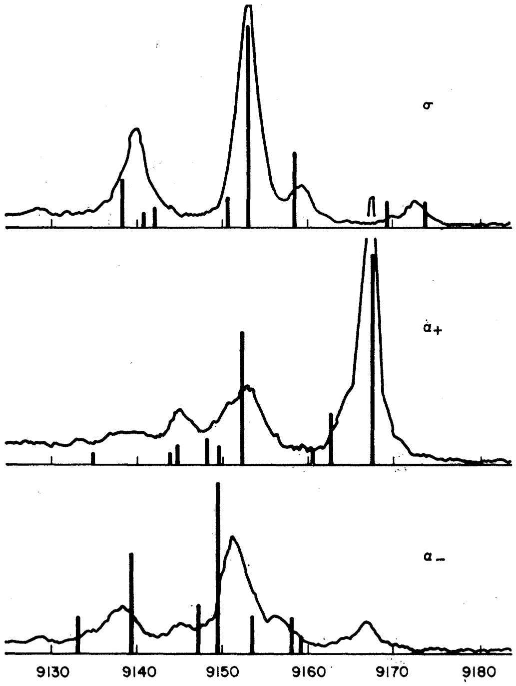

FIG. 7. Zeeman spectra at 5°K, with $H=70$ kG$\|\langle 001\rangle$, compared with a calculation which ignores the Jahn-Teller effect.

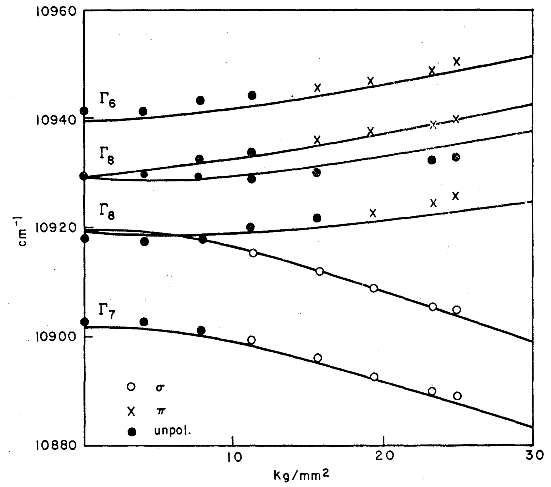

FIG. 9. Effect of uniaxial stress approximately parallel to $\langle 001\rangle$ on the ${}^4T_2$ term of KMgF$_3$:V^{2+}. The full lines are calculated including the effect of Jahn-Teller interaction. The predominant polarization of transitions from the ${}^4A_2$ ground term is indicated.

splittings as a function of stress is shown in Fig. 9. A uniform shift of 0.70 cm^{-1}/(kg/mm^2) has been subtracted from these data. (This shift is due to the hydrostatic component of the strain, and implies a logarithmic derivative of Δ with respect to internuclear separation of 4.2. The point-charge model predicts 5, if local relaxation is neglected.)

In Fig. 9 we compare the observed line positions, and in Fig. 10 the intensities, with the theory of Sec. 2, taking u in Eq. (6) to be -1.5 cm^{-1}/(kg/mm^2) to obtain the best fit. This is to be compared with -1.1 ± 0.3 cm^{-1}/(kg/mm^2) obtained from spin resonance in the ground state.[22] The discrepancy is within experimental error; Jahn-Teller mixing of the ${}^4T_2$ and ${}^4T_1$ terms is clearly unimportant, as expected.

The stress data are the only ones at all sensitive to the second-order terms in the Ham theory. If these are neglected, the stress splitting of the upper Γ_8 level almost disappears. Unfortunately, as can be seen from Fig. 10, this splitting is not fully resolved and is difficult to measure accurately. Consequently the effective value of $\hbar\omega$, on which the size of the second-order terms depends [see Eq. (5)] cannot be found with any accuracy.

A word on the relation between our fitted values of x, u, and $\hbar\omega$, of which the first two are reasonably accurate, but the third is more or less arbitrary. If we assume that the interatomic forces in KMgF$_3$ are unaltered in the region of the impurity ion, and that local and macroscopic strains are identical, V in (3) is related to u by $V=\sqrt{6}u(c_{11}-c_{12})/3R$, where R is the interatomic spacing. Substituting $u=1.1$ cm^{-1}/(kg/mm^2),

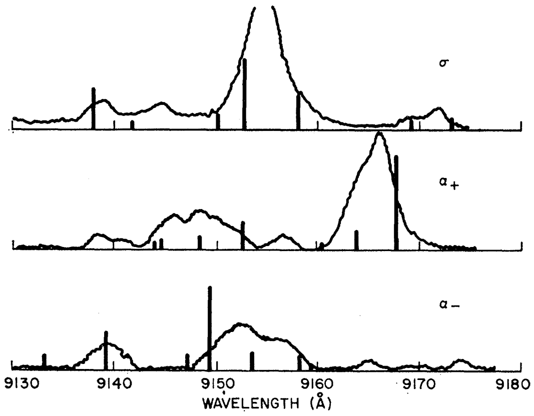

FIG. 8. Same as Fig. 7, with $T=10$°K, $H\|\langle 111\rangle$.

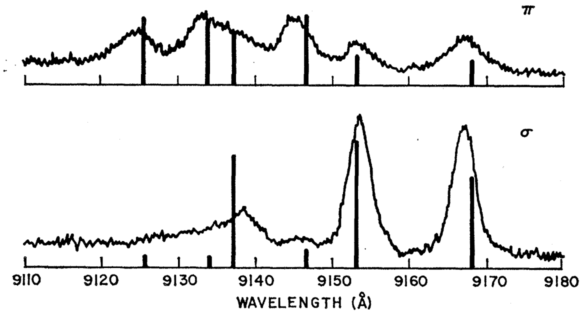

FIG. 10. Absorption spectrum of KMgF$_3$:V^{2+} under a stress of 16 kG/mm^2 parallel to $\langle 001\rangle$.

$R=2.0$ Å, $c_{11}-c_{12}=9.4\times10^3$ kg/mm^2,[26] $\mu=3.1\times10^{-23}$ g (one fluorine mass) and $x=2.6$ in $\hbar\omega=(3\hbar^2V^2/2\mu x)^{1/3}$, we find $\hbar\omega=260$ cm^{-1}. This value would be quite consistent with our data.

5. CONCLUSIONS

We have subjected the first-order theory of the Ham effect to an extremely searching test. We find that it will account in detail for the spin-orbit splitting and Zeeman effect of the lowest vibronic level of the $^4T_2$ term of V^{2+} in KMgF$_3$. The residual discrepancies, typically 10%, between theory and experiment are no larger than those commonly found in crystal-field problems. There is only one completely arbitrary parameter, x; the other parameters, k and $\hbar\omega$, are given approximately by other data and anyway have almost negligible effect on the calculated results.

The splitting and shift of the levels under ⟨001⟩ stress can be accounted for, to the same order of accuracy, with the introduction of two further parameters. These represent the matrix elements for A_{1g} (hydrostatic) and E_g (tetragonal) strain, and the fitted values are close to those expected theoretically.

We have been unable to check the prediction of the Ham theory that trigonal fields are quenched like the spin-orbit coupling. This is partly because of experimental difficulties, but primarily because we have no independent measure of the unquenched trigonal field produced by ⟨111⟩ stress (the ground-state splitting, measured by spin resonance in Ref. 22, gives no information about the splitting of $^4T_2$).

There are two conditions for the validity of the version of the Ham theory given here. The first is that the Jahn-Teller interaction must be strong relative to the spin-orbit coupling and other perturbations,[27] but not so strong as to mix different cubic terms.[28] Symbolically, $\mathcal{H}_{\rm eff}, \mathcal{H}_{\rm pert} \ll \mathcal{H}_{\rm JT} \ll \mathcal{H}_{\rm FI}, \mathcal{H}_{\rm cub}$. These conditions are well satisfied in the $^4T_2$ term of KMgF$_3$:V^{2+}, as in many other transition-metal ion systems. The other condition is that there be significant coupling only to E_g vibrations. This is to be expected in octahedra systems, and the good fit to theory shows that it holds for V^{2+} in KMgF$_3$.[29] It is difficult to see why the situation should be so different for the same ion in MgO.[10]

It should be emphasized that only the first-order theory of the Ham effect has been checked quantitatively. While the stress data confirm that second-order terms have the correct qualitative effect, quantitative comparison is not possible. However, within its limitations, the present experiment forms the most thorough check on the correctness of Ham's theory that has yet been made.

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[26] H. M. Rosenberg and J. K. Wigmore, Phys. Letters **24A**, 317 (1967).

[27] Recently, an alternative treatment for the case $\mathcal{H}_{\rm JT} \lesssim \mathcal{H}_{\rm eff}$ has been put forward by F. S. Ham, W. M. Schwartz, and M. C. M. O'Brien [Bull. Am. Phys. Soc. **14**, 390 (1969); Phys. Rev. **185** 548 (1969)] to account for the far infrared, E.P.R., and Mössbauer spectra of MgO:Fe^{2+}.

[28] A. M. Stoneham and M. Lanoo [J. Phys. Chem. Solids **30**, 1769 (1969)] have treated the case of terms so close that this approximation cannot be made.

[29] As far as the spin-orbit splittings and Zeeman effect are concerned, some of the quenching could be attributed to interaction with T_{2g} vibrations without affecting agreement with experiment. (The ρ term in $\mathcal{H}_{\rm eff}$ would be slightly quenched, but this effect might be difficult to detect.) However, the fact that the splitting under ⟨001⟩ stress is as large as calculated shows that the T_{2g} interaction is not important.