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Absence of a strong Jahn-Teller effect in the $^4T_{2g}$ excited state of V^{2+} in MgO

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We have measured the Zeeman spectrum of the $^4A_{2g} \rightarrow {}^4T_{2g}$ zero-phonon lines of V^{2+} in MgO using high magnetic fields and low temperatures. The data conclusively demonstrate that the splitting and structure within the zero-phonon lines (at zero field) arises from spin-orbit splitting in the $^4T_{2g}$ state. It is shown that the marked deviation of the spectrum from that predicted by crystal-field theory *cannot* be accounted for in terms of the usual Jahn-Teller models.

INTRODUCTION

The optical absorption associated with the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of V^{2+} in MgO has been reported by Sturge.[1] At the origin of the band there are two zero-phonon lines each with a half-width of ~20 cm^{-1} and separated from each other by 40 cm^{-1}; the lower-energy line is a factor of 3 stronger in intensity than the higher-energy one. The spectrum contrasts markedly with the spectrum of the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition of V^{2+}-doped $KMgF_3$,[2] where there are four zero-phonon lines separated from each other by 11 to 15 cm^{-1}, each with half-widths of ~3 cm^{-1}. These four lines have been shown from magnetic-field and uniaxial-stress measurements to arise from transitions to the four spin-orbit levels of the $^4T_{2g}$ state. The spin-orbit splitting in $KMgF_3$ is less than that predicted by crystal-field theory, but the reduction can be understood on the basis of Ham's theory[3] of the quenching of off-diagonal operators by the dynamic Jahn-Teller effect. The effect of uniaxial stress on the $^4A_{2g} \rightarrow {}^4T_{2g}$ zero-phonon lines of $MgO:V^{2+}$ was also studied,[1] including measurements with the stress along the ⟨111⟩ crystallographic direction. The zero-phonon lines were displaced in energy but no splitting or polarization was observed. This suggested that there was complete quenching of the stress operator of T_{2g} symmetry, which would arise if the Jahn-Teller effect were strong. It was consequently considered that the zero-phonon line structure arose in some way from a strong Jahn-Teller effect, but was entirely different in origin to that giving the four lines in $KMgF_3:V^{2+}$. Several explanations for the structure of the zero-phonon line have been advanced, based on this assumption of a strong Jahn-Teller effect,[1,4-7] but the experimental data available to date are unable to distinguish between the various models. The origin of the structure of zero-phonon line is then still in question and we, therefore, aim to reinvestigate this problem.

For $KMgF_3:V^{2+}$ the $^4A_{2g} \rightarrow {}^4T_{2g}$ zero-phonon lines are sufficiently narrow that a direct measure of the Zeeman splitting was possible. In $MgO:V^{2+}$ the $^4A_{2g} \rightarrow {}^4T_{2g}$ zero-phonon lines were found to be considerably broader; furthermore, their extreme weakness made Zeeman measurements impracticable. However, it is now possible, with a combination of high fields and low temperatures, to measure the polarization of the lines by the sensitive MCD (magneto-circular dichroism) technique, and this can provide invaluable new information on which to base an interpretation of the zero-phonon line structure. In this paper we report on the Zeeman spectrum measured at a magnetic field of 5 tesla and a crystal temperature of 1.6 K, and it will be shown that on the basis of these new data the nature of the zero-phonon line splitting can be firmly established. Viliani *et al.*[8] have recently reported on the circular polarization of the $^4A_{2g} \rightarrow {}^4T_{2g}$ zero-phonon lines in a magnetic field of 5 tesla. However, higher temperatures (4.2 K) and much poorer resolution were used, and deductions, although consistent with ours, were not conclusive.

EXPERIMENT

The crystal samples were first heated in vacuum at 1400 °C for ten hours to increase the concentration of V^{2+} ions. This produces less deterioration of crystal quality than the H_2 anneal used by Sturge.[1] The V^{2+} concentration so obtained was sufficiently high that conventional absorption techniques could be used without interference from the V^{3+} spectrum. This gave somewhat better signal-to-noise ratios than the excitation technique used in other work.[1,8] The zero-field spectrum is shown in Fig. 1. The "double" peak is obvious, but it is noted there is also a very clear shoulder

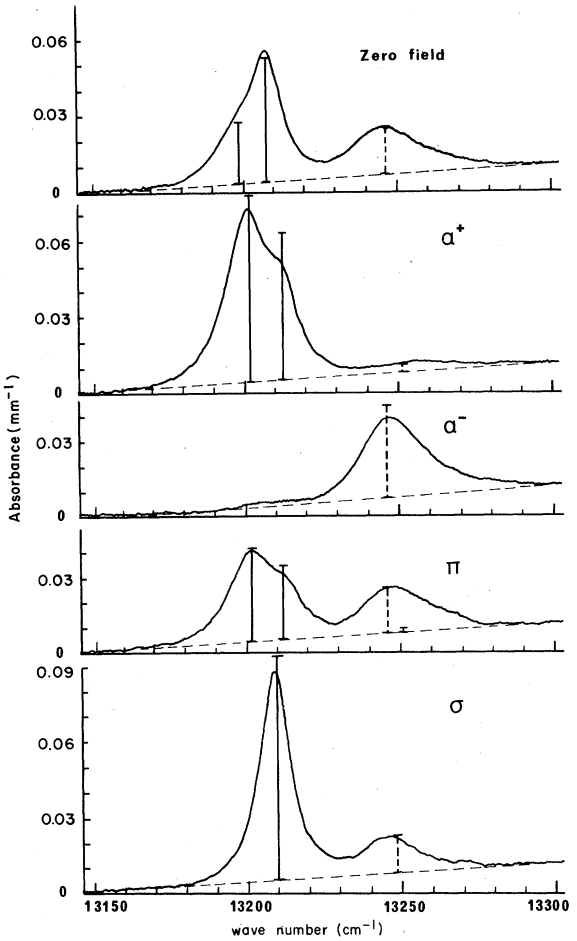

FIG. 1. Polarized absorption spectra for the $^4A_2 \rightarrow {}^4T_2$ no-phonon transition of V^{2+} in MgO at 1.6 K in zero field and in a magnetic field of 5 tesla. The vertical lines show the predicted line intensities. The broken lines have been reduced in length by a factor of four, relative to the solid lines.

on the low-energy side of the lower line. This shoulder is apparent at much higher temperature (~50 K) and is visible because of the better quality of the crystals used here compared to previous measurements.[1,8] The spectrum is, therefore, seen to consist of at least three lines with relative energies of −11, 0, and 40 cm^{-1} and approximate relative intensities $0.4 \pm 0.1, 1, 0.5 \pm 0.1$.

The Zeeman spectrum for a field of 5 tesla along the ⟨001⟩ direction is shown in Fig. 1. The spectrum for a field along the ⟨111⟩ direction is very similar, and the reasons for this will be discussed later. A crystal temperature of 1.6 K was used, so that at 5 tesla only the lowest spin projection $M_S = -\frac{3}{2}$ of the $^4A_{2g}$ ground state has appreciable population, and all spectral lines in Fig. 1 arise from transitions from that state. The magnetic-dipole transitions are spin allowed, and consequently the spin projection in the excited state will also be $M_S = -\frac{3}{2}$. The orbital component of the excited state will be determined by the polarization of the magnetic vector of the incident light. The polarized Zeeman spectrum, therefore, gives direct information about the excited state wave functions. For example, the very strong circular polarization exhibited by the experimental traces indicates that the lower-energy component of the "doublet" has associated with it wave functions of the form $|\gamma = +1; M_S = -\frac{3}{2}\rangle$ (where γ denotes the orbital component of the T_{2g} state) with very little contribution from wave functions of the form $|\gamma = -1; M_S = -\frac{3}{2}\rangle$.

For the upper component of the doublet, 40 cm^{-1} higher in energy, the situation is the reverse. This separation in energy of the states involving $|\gamma = +1; M_S = -\frac{3}{2}\rangle$ and $|\gamma = -1; M_S = -\frac{3}{2}\rangle$ can only arise from spin-orbit splitting. We will show in the next section that the polarization of the three-zero-phonon lines is what is expected for transitions to the spin-orbit levels of the $^4T_{2g}$ state.

DISCUSSION

In first order, spin-orbit interaction splits the $^4T_{2g}$ state into three levels with Γ_7 lowest, followed in increasing energy by a $^{3/2}\Gamma_8$, and then a degenerate Γ_6 and $^{5/2}\Gamma_8$. The $^4A_{2g} \rightarrow {}^4T_{2g}$ magnetic-dipole selection rules can be readily obtained from the O_h tables of Griffith[9] and the suffix notation for the Γ_8 irreducible representations are as used in these tables. The system, however, exhibits features of the full rotation group and it is instructive in understanding the isotropy of the Zeeman pattern to obtain the selection rules in this context. The first-order spin-orbit splitting of a $^4T_{2g}$ state can be obtained using operator-equivalent techniques and will be similar to the splitting of a ^4P atomic term. The selection rules for a $^4A_{2g} \rightarrow {}^4T_{2g}$ transition are then the same as those for a $^4S \rightarrow {}^4P$ atomic system where clearly there will be no dependence on the direction of the magnetic field. The selection rules for the $^4A_{2g} \rightarrow \Gamma_7$, $^4A_{2g} \rightarrow {}^{3/2}\Gamma_8$, and $^4A_{2g} \rightarrow \Gamma_6 + {}^{5/2}\Gamma_8$ are the same as those for the $^4S_{3/2} \rightarrow {}^4P_{1/2}$, $^4S_{3/2} \rightarrow {}^4P_{3/2}$, and $^4S_{3/2} \rightarrow {}^4P_{5/2}$, respectively, and they can be obtained using ordinary Clebsch-Gordan coefficients. The predicted intensity of transitions from the lowest-two components of the ground state is shown in Fig. 2. The line position in a magnetic field can also be calculated from the g values of the ground and excited states. The g value of the ground state is 1.98 (Ref. 10) (equivalent to that of ^4S). Those of the $^4T_{2g}(t^2e)$ are equivalent to those of the ^4P if the orbital angular momentum is taken[11] as $\frac{1}{2}$ (neglecting for the mo-

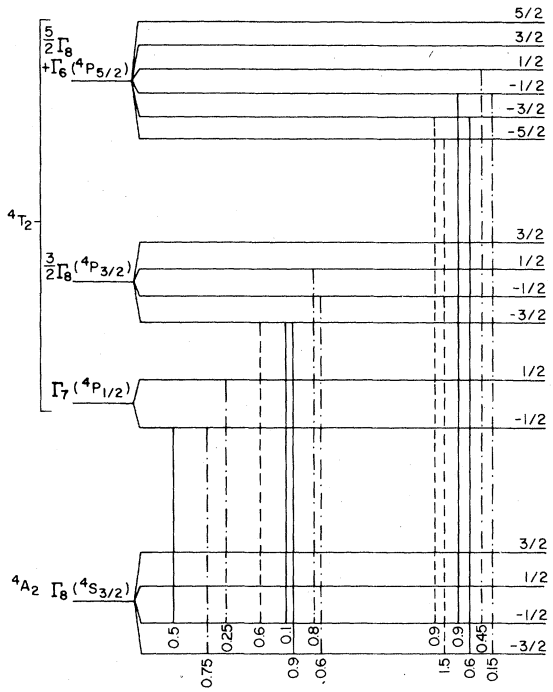

FIG. 2. Predicted relative transition probabilities for magnetic-dipole transitions from $^4A_2 \rightarrow {}^4T_2$, obtained by using the P-T equivalence. For clarity only those from the ground $M_S = -\frac{3}{2}$ and $M_S = -\frac{1}{2}$ states are shown. ——σ, ---α^-, — · —α^+.

ment covalency and the quenching of orbital angular momentum by the Jahn-Teller effect). The spectrum in the low-temperature limit has been calculated and is shown by the vertical lines in Fig. 1. It can be seen that this gives an excellent account of the polarized Zeeman spectrum. One serious discrepancy, however, is the weakness of the total transition intensity to the highest spin-orbit level $\Gamma_6 + {}^{5/2}\Gamma_8$ compared with that to the lower spin-orbit levels $\Gamma_7 + {}^{3/2}\Gamma_8$. They are predicted to be equal but there is a factor-of-3 difference. This disagreement is particularly marked in the α^- spectrum, and will be discussed later.

Incidentally, the very existence of an α^- transition rules out the possibility that the lines have been misassigned, and really belong to the $^4A_2 \rightarrow {}^2T_1$ transition.

Second-order spin-orbit interaction affects the position of all four $^4T_{2g}$ levels and the degeneracy of the Γ_6 and $^{5/2}\Gamma_8$ levels will be lifted. However, the important effect as far as Zeeman selection rules are concerned is the admixture of the $^{3/2}\Gamma_8$ and $^{5/2}\Gamma_8$ wave functions. The result of appreciable mixing would be a change in the predicted polarization of the Zeeman lines and in particular the circular polarization of the lines would be directly affected. However, the lines are observed to be almost totally circularly polarized. For transition to the lower Γ_8 level the ratio of left to right circular polarization is in excess of 50:1, which implies that mixing of the $^{3/2}\Gamma_8$ and $^{5/2}\Gamma_8$ wave functions is less than 15%. This is consistent with the full crystal-field calculation, which gives ~10% mixing of the $^{3/2}\Gamma_8$ and $^{5/2}\Gamma_8$ basis functions arising from second-order spin-orbit interaction ~10%. Clearly, however, there is no appreciable extra mixing of the $^{3/2}\Gamma_8$ and $^{5/2}\Gamma_8$ by any other interaction, including Jahn-Teller interaction.

The presence of a weak dynamic Jahn-Teller effect is suggested by the fact that the experimentally observed spin-orbit splitting is somewhat smaller than that predicted by a full crystal-field calculation. Experimentally the positions of the levels (relative to the strongest peak at 13 210 cm^{-1}) are as follows: $\Gamma_7(-11\ cm^{-1})$, $^{3/2}\Gamma_8(0\ cm^{-1})$, $^{5/2}\Gamma_8(40\ cm^{-1})$, and $\Gamma_6(40\ cm^{-1})$. The uncertainty in the position of the Γ_7 level is of the order of ± 1 cm^{-1}. The $^{5/2}\Gamma_8$ and Γ_6 are not resolved and the uncertainty in their position is consequently large, ± 5 cm^{-1}. A crystal-field calculation[11] with $B = 550$ cm^{-1}, $C = 2475$ cm^{-1}, $Dq = 1320$ cm^{-1}, and $\zeta = 120$ cm^{-1} (Ref. 12) gives $\Gamma_7(-30\ cm^{-1})$, $^{3/2}\Gamma_8(0\ cm^{-1})$, $^{5/2}\Gamma_8(51\ cm^{-1})$, and $\Gamma_6(58\ cm^{-1})$. The absence of mixing between $^{3/2}\Gamma_8$ and $^{5/2}\Gamma_8$ indicates that if there is any Jahn-Teller effect it must be weak. This suggests that the perturbation approach of Ham *et al.*[13] is the most appropriate model to try, since it gives results in simple analytic form. We shall see that diagonalization of the spin-orbit matrix gives essentially the same results.

We can simplify the calculation by neglecting the coupling to t_{2g} vibrations, since the stress data show[1] that the coupling to e_g strain is at least an order of magnitude stronger than to t_{2g}. Adapting the Ham *et al.* calculation to the case of $^4T_2$, we find for the shifts of each level (relative to the centroid of the term):

$$\Delta E(\Gamma_6) = -E_{JT}\left(\frac{1}{10} + \frac{9\hbar\omega}{10\hbar\omega + 25\lambda}\right),$$

$$\Delta E(^{5/2}\Gamma_8) = -E_{JT}\left(\frac{37}{100} + \frac{9\hbar\omega}{50\hbar\omega + 125\lambda} + \frac{9\hbar\omega}{20\hbar\omega + 80\lambda}\right),$$

$$\Delta E(^{3/2}\Gamma_8) = -E_{JT}\left(\frac{8}{25} + \frac{63\hbar\omega}{100\hbar\omega - 250\lambda} + \frac{\hbar\omega}{20\hbar\omega + 30\lambda}\right),$$

$$\Delta E(\Gamma_7) = -E_{JT}\left(\frac{\hbar\omega}{10\hbar\omega - 15\lambda} + \frac{9\hbar\omega}{10\hbar\omega - 40\lambda}\right).$$

Here E_{JT} is the energy depression of $^4T_2$ due to the Jahn-Teller effect, in the absence of spin-orbit coupling, ω is the effective phonon frequency, and $\lambda\ (= -\zeta/6)$ is the coefficient of $\vec{L} \cdot \vec{S}$ in the effec-

tive Hamiltonian for $^4T_2$. Second-order terms in E_{JT} are neglected in these expressions. Since, for V^{2+} in MgO, $|\lambda| \ll \hbar\omega$ the expressions simplify to[14]:

$$\Delta E(\Gamma_6) = \Delta E(^{5/2}\Gamma_8) = 9E_{JT}\,\lambda/4\hbar\omega - E_{JT}\ ,$$

$$\Delta E(^{3/2}\Gamma_8) = -3E_{JT}\,\lambda/2\hbar\omega - E_{JT}\ ,$$

$$\Delta E(\Gamma_7) = -15E_{JT}\,\lambda/4\hbar\omega - E_{JT}\ .$$

Taking $\lambda = -22$ cm^{-1} we can fit the $^{5/2}\Gamma_8 - {}^{3/2}\Gamma_8$ splitting of 40 cm^{-1} (which is the best established experimentally) with $E_{JT}/\hbar\omega = 0.13$, an extremely small value, justifying our perturbation approach. While the value of $E_{JT}/\hbar\omega$ which gives the best fit can vary from zero to 0.22, according to the precise value taken for ζ in the crystal-field calculation, this qualitative conclusion is not affected.

The additional $^{5/2}\Gamma_8 - {}^{3/2}\Gamma_8$ mixing due to the Jahn-Teller interaction calculated for the above parameters is less than 5%, as observed. However, here the agreement ends. The $^{3/2}\Gamma_8 - \Gamma_7$ splitting, observed to be 11 cm^{-1}, is calculated to be 22 cm^{-1}, and no adjustment of parameters (in particular, variation of J from 90 to 140 cm^{-1}, i.e., from 60% to 90% of the free-ion value, while $E_{JT}/\hbar\omega$ is chosen to fit the $^{5/2}\Gamma_8 - {}^{3/2}\Gamma_8$ splitting) can reduce this discrepancy appreciably. Nor can the theory account for the small relative intensity of the transition to $^{5/2}\Gamma_8 + \Gamma_6$, predicted to be more than three times that observed. Finally, the absence of any observable splitting under $\langle 111 \rangle$ stress[1] is totally inexplicable: The trigonal field induced by stress is known from other measurements and, like the spin-orbit interaction, should be reduced only by 25% by this weak Jahn-Teller interaction.

Essentially the same discrepancies are found if one uses the theoretical approach of Ham,[3] adapted by Sturge,[2] in which $\lambda/\hbar\omega$ rather than $E_{JT}/\hbar\omega$ is the expansion parameter. Figure 3 shows the result of such a calculation. The impossibility of fitting the observed $^{5/2}\Gamma_8 - {}^{3/2}\Gamma_8$ and $^{3/2}\Gamma_8 - \Gamma_7$ splittings simultaneously is obvious. We conclude that the anomalous splitting and intensities of the $^4T_2$ term in MgO:V^{2+} cannot be understood in terms of the normal dynamic or static Jahn-Teller models.

The standard model is based on the assumption that the impurity ion in the solid can be approximated by an octahedral cluster with a single discrete E_g mode. It seems unlikely that the mere introduction of additional discrete modes with $\hbar\omega \gg |\lambda|$ can greatly affect our qualitative conclusions. Appreciable coupling to a continuum of low-frequency acoustic modes would certainly affect it, since the perturbation approach would no longer be valid. It would, in fact, no longer make sense to

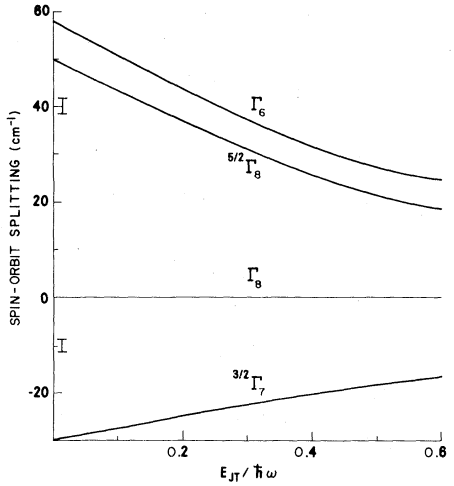

FIG. 3. Spin-orbit splitting of the zero-phonon level of a $^4T_2$ term as a function of Jahn-Teller interaction calculated as in Ref. 2. Parameters: ζ:120 cm^{-1}, $\hbar\omega$ = 200 cm^{-1}. The splittings scale roughly as ζ and are insensitive to $\hbar\omega$. The vertical bars indicate the experimental data.

talk of "no-phonon lines." Since it has been shown[1] that these transitions are magnetic dipole in character and that there is only weak absorption in the frequency range just above them, the effects must be weak and it would be surprising if they could account for the present discrepancies. If, however, the low-frequency modes must be considered, the model would be complex and a substantial departure from the cluster model.

The relative intensities of the zero-phonon lines observed in Jahn-Teller systems have been treated recently by Montagna *et al.*[15] These authors have have made a more complete calculation still within the cluster model and have shown that there are corrections to be made to the predicted intensities. The intensities of the transitions to the higher spin-orbit components of a multiplet are reduced relative to the lower-energy components. This is in qualitative agreement with observed trend. They have taken the example of the $^4T_{2g}$ term of $KMgF_3:V^{2+}$ and have shown that the 50% reduction in the higher-order spin-orbit components can be explained in this way.[15] However, the observed intensities often show substantially larger departures from theory in $KMgF_3:V^{2+}$. For example, in the $^5T_{2g}$ of MgO: Fe^{2+} (Ref. 2) in the $^3T_{2g}$ of MgO: Ni^{2+} (Ref. 16) and in the $^4T_{2g}$ of $Cs_2SiF_6:Mn^{4+}$ (Ref. 17) systems the higher spin-orbit components are too weak to see. Treatments within a cluster model cannot explain such observations. Likewise the large change in the relative intensities found in the MgO:V^{2+} system cannot be wholly accounted for by the corrected intensity calculation. This

latter aspect is not surprising since the cluster model itself is inadequate in predicting the energy of the spin-orbit levels of the system.

The absence of any splitting of the zero-phonon lines with a $\langle 111 \rangle$ uniaxial stress has recently been confirmed by experiments by Boyrivent *et al.*[18] They have in addition shown that there is no overall dichroism produced in the $^4A_{2g} \rightarrow {}^4T_{2g}$ absorption band and it can be concluded that the $^4T_{2g}$ state is unaffected by the trigonal deformation quite apart from Jahn-Teller quenching.[19-21] The trigonal stress is, however, observed to split the ^2E_g level, and straightforward crystal-field analysis predicts that observable splitting within the $^4T_{2g}$ state should result.[1] The fact that there is none is disturbing. A corresponding analysis of the $^4T_{2g}$ term of Mn^{4+} (isoelectronic with V^{2+}) in trigonal Cs_2TiF_6 has been made.[22] The trigonal field splitting of the $^4T_{2g}$ state as deduced from the observed ^2E_g splitting is in good agreement with the observed $^4T_{2g}$ splitting when allowance is made for the Jahn-Teller quenching, showing that in this case the model is self-consistent. The discrepancy for an externally applied trigonal field in the $MgO:V^{2+}$ system is inexplicable. A possibly related anomaly exists, however, in the $^3T_{2g}$ term of Ni^{2+} in MgO (Ref. 23). The splitting by $\langle 111 \rangle$ uniaxial stress is a factor-of-10 smaller than that predicted by crystal-field analysis, while there is no reduction in the $\Gamma_4 - \Gamma_3$ spin-orbit separation compared with that given by a full crystal-field calculation. This situation is inconsistent with the predictions of a cluster model.

We conclude that in spite of the great success of the cluster model with a dynamic Jahn-Teller effect in accounting for the splitting of no-phonon lines there remain discrepancies between theory and experiment which have yet to be resolved.

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