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Dynamic Jahn-Teller Effect in the $^3T_2$ Excited Term of $Al_2O_3:V^{3+}$

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We report high-resolution measurements of the structure near the electronic origin of the $^3T_1 \rightarrow {}^3T_2$ absorption band of V^{3+} in Al_2O_3. The structure is explained in terms of Ham's theory of the dynamic Jahn–Teller effect. The trigonal field of Al_2O_3 is partially quenched, being effectively reduced by a factor of 45 in the lowest vibronic level of the Jahn-Teller distorted $^3T_2$ term. First-order spin-orbit coupling is quenched, but second-order effects arising from interaction with other terms of the d^2 configuration are important. This is the first reported observation of the quenching of off-diagonal operators (the "Ham effect") other than angular momentum. The anomalous splitting of the $^3T_1 \rightarrow {}^3T_2$ band maximum is discussed, but no very satisfactory explanation is found.

1. INTRODUCTION

THE optical spectrum and magnetic properties of $Al_2O_3:V^{3+}$ are in the main well explained by conventional crystal-field theory.[1,2] However, the structure of the first spin-allowed absorption band, $^3T_1 \rightarrow {}^3T_2$, is not explicable on this basis.[3] This difficulty applies particularly to the sharp line structure on the low-frequency side of the band, in the region 15850-15900 cm^{-1}. McClure[3] pointed out that these lines are most likely no-phonon transitions to a Jahn-Teller distorted $^3T_2$ state. Subsequently, Ham[4] has worked out the properties of a triply degenerate state suffering a Jahn-Teller distortion. He finds that off-diagonal operators, such as orbital momentum, spin-orbit coupling or (in the case of tetragonal distortion, which is the usual kind) trigonal fields, can be partially or totally quenched, according to the strength of the Jahn-Teller interaction. We will call this quenching the Ham effect. The only available data with which Ham could compare his theory were the results of spin-resonance measurements, in which great reductions in the orbital contributions to g factors were seen; but a more dramatic consequence of the Ham effect is a drastic alteration in energy-level separations, which can best be observed by optical spectroscopy. This paper reports the first identification of such effects in optical spectra.

The crystal-field levels of the d^2 ion V^{3+} in a trigonally distorted octahedral environment are sketched in Fig. 1. Jahn-Teller effects are ignored in this figure. On the right are the observed energy levels in $Al_2O_3:V^{3+}$.[1,3] There is no sign of a Jahn-Teller effect in the lowest cubic field term,[5] $^3T_1(t_2{}^2)$. The g values and spin-orbit splitting of the $^3\hat{A}$ ground level,[6] and the overall splitting of the term, are in excellent agreement with the predictions of crystal field theory.[2] Crystal field theory[1,2] also predicts rather accurately the positions of the observed excited states, except for those derived from the $^3T_2$ term.

The general appearance of the band arising from the $^3T_1(^3\hat{A}) \rightarrow {}^3T_2$ transition has been described by McClure.[3] There are three noteworthy features: first, the absence of any appreciable trigonal splitting (what splitting there is between the maxima of the π- and σ-polarized bands is in the opposite sense to that predicted). Second, a relatively sharp line at about 15880 cm^{-1} (the low-energy extremity of the band), appearing equally strongly (though at slightly different positions) in both polarizations. Third, a pronounced vibrational progression based on the origin line; some nine distinct transitions are seen with a mean interval of 200 cm^{-1}. McClure[3] demonstrated that the sharp lines mark the true electronic origin of the $^3T_1 \rightarrow {}^3T_2$ transition, i.e., they arise from no-phonon transitions. He pointed out that the appearance of σ- and π-polarized origins within a few cm^{-1} of each other is in itself evidence of Jahn-Teller distortion in the $^3T_2$ term. If there were no distortion, the σ-polarized origin would be some 400 cm^{-1} above the π, and would presumably be lost in the band, McClure's picture is of a static Jahn-Teller effect, which completely quenches the trigonal field and first order spin-orbit splitting. The no-phonon line should then be a doublet, having a second-order spin-orbit splitting which he calculated to be about 1 cm^{-1}. As the spin is quantized along the direction of tetragonal distor-

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[1] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. **26**, 34 (1958); W. Low, Z. Physik. Chem. (Frankfurt) **13**, 107 (1957).

[2] R. M. Macfarlane, J. Chem. Phys. **40**, 373 (1964).

[3] D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

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

[5] The Jahn-Teller effect is expected to be weak in the $t_2{}^2$ configuration; furthermore, the trigonal splitting is large, bringing a Jahn-Teller resistant orbital singlet lowest.

[6] Symbols with carets indicate representations of the trigonal group C_3.

tion, both lines should appear in both polarizations. We have studied these lines in greater detail, and find much more structure than predicted by McClure; it is strongly polarized.

In Sec. 2 we describe our measurements of this sharp line structure. In Sec. 3 we show that our results are in good agreement with the qualitative predictions of Ham's theory. The splitting due to the trigonal field of Al_2O_3 is partially quenched but is still well resolved. The dominance of second-order spin-orbit splitting over first order, also predicted by Ham, is demonstrated. These second-order effects arise primarily from interaction with levels outside the $^3T_2$ term. The absence of trigonal splitting in the $^3T_1 \rightarrow {}^3T_2$ band maximum is discussed; while this is presumably a consequence of the Jahn-Teller effect a full explanation is not yet forthcoming.

2. EXPERIMENTAL

A. Procedures

The sample used was of approximately 0.02% V^{3+} doping and was 60 mm² in cross-sectional area and 7 mm thick. It was oriented and ground so that the *c* axis lay in the plane perpendicular to the direction of impinging light. This light beam passed in order through a focusing lens, a polaroid, the cryostat and masked-off sample, and finally focused on the spectrometer entrance slits. Phototube signals were amplified and then either recorded on a chart recorder if signal-to-noise ratio was sufficiently high, or entered into a multichannel digital memory bank if greater sensitivity was desired. In the latter case, several identical scans were entered, whereupon the cumulative signal was displayed on an oscilloscope and photographed.

The light source used was a GE-1493 tungsten filement bulb powered by a stabilized dc power supply. The spectrometer was a model No. 1700 Czerny-Turner manufactured by Spex Industries, Inc. This instrument is equipped with a 2160 line/mm grating and has an effective resolving power of 10^5. The phototube was an EMI-5504 Q(S-20) which at room temperature gave a dark current of less than 10^{-9} A. For single scans a Leeds and Northrup 9836 A dc amplifier and pen recorder were used to record the signals. For repeated scans a Hewlett-Packard 425A micro-ammeter was used for dc amplification, and its output fed into the digital memory bank. This instrument, the model ND 800 "Enhancetron" manufactured by Nuclear Data, Inc. effectively improves the signal-to-noise ratio by the square root of the number of scans taken.

The sample was cooled by conduction to a 2.0°K liquid-helium bath and could be warmed by a magnanin wire heater wound around it. The conduction was through a 10-mm-long by 1-mm-diam oxygen-free high-conductivity copper cylinder, one end of which was attached to the crystal by a vacuum-evaporation technique. This arrangement not only permitted the sample temperature to be raised by as much as 10°K with a relatively small heater input ($<\frac{1}{3}$ W), but also eliminated all difficulties connected with passing light through liquid refrigerants.

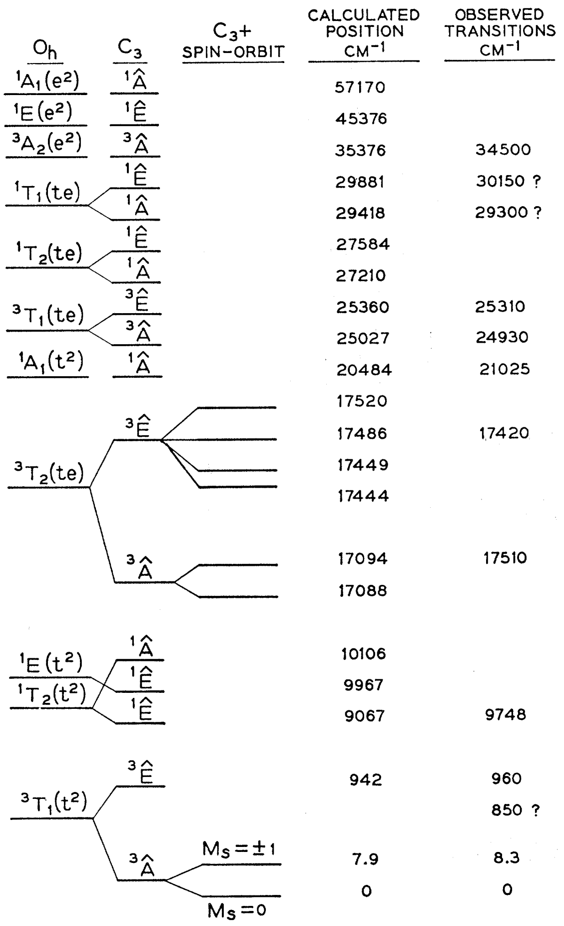

FIG. 1. Energy-level scheme for V^{3+} in a trigonally distorted octahedral environment. The left-hand column gives the cubic terms; the second column shows the splitting of some of these terms in a trigonal field (C_3); the third shows some spin-orbit splittings, and the fourth, the calculated positions of the levels shown (Macfarlane, Ref. 2). The parameters used in the calculations are: $B=610$ cm^{-1}, $C=2500$ cm^{-1}, $10Dq=18000$ cm^{-1}, $\zeta=155$ cm^{-1}, $v'=\langle t_2+|V_{\text{trig}}|e+\rangle=200$ cm^{-1}, $v=-3\langle t_2+|V_{\text{trig}}|t_2+\rangle=800$ cm^{-1}. On the right are the observed positions of absorption lines and band maxima in Al_2O_3; queries indicate doubtful assignments.

Temperature was inferred from the absorption strengths of the sharp $^3T_1(^3\hat{A}) \rightarrow {}^1A_1(t_2^2)$ doublet which occurs around 4757 Å. Comparison of the intensity ratio of this doublet with the result of measurements made with the crystal immersed in liquid refrigerants at 20°K, 4.2 °K, and 2.0 °K yielded the population ratio of the ground states and thus the temperature. These measurements also confirm the ground-state splitting to be 8.3 ± 0.05 cm^{-1},[7] rather than 7.85 cm^{-1}.[8]

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[7] S. Sakatsume and I. Tsujikawa, J. Phys. Soc. Japan **19**, 1080 (1964).

[8] S. Foner and W. Low, Phys. Rev. **120**, 1585 (1960).

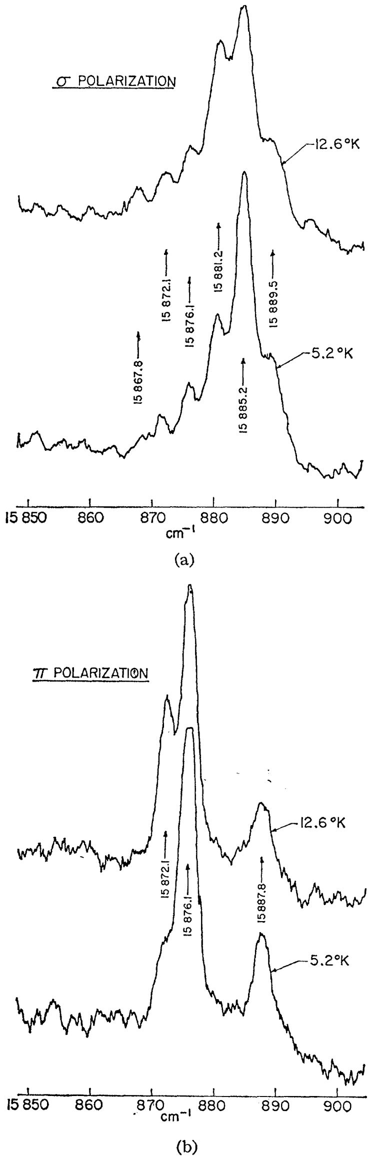

FIG. 2. Absorption of Al$_2$O$_3$:V^{3+} in the range 15850–15900 cm^{-1}. (Vertical scale arbitrary, but the same for all curves.) (a) σ polarization: upper trace, 12.6 °K; lower trace, 5.2 °K. (b) π polarization: upper trace, 12.6 °K; lower trace, 5.2 °K.

B. Results

Experimental traces, taken at 5.2° and 12.6°K in σ and π polarization of absorption in the region of the no-phonon $^3T_1(^3\hat{A})\rightarrow{}^3T_2$ transition, are shown in Fig. 2. Those lines which decrease with increasing temperature evidently originate from the ground ($M_s=0$) state of the $^3\hat{A}$ level, and those which increase with increasing temperature evidently originate from the $M_s=\pm1$ states, which lie 8.3 cm^{-1} higher in energy. We see that the only two features not clearly demonstrated by these traces are: (i) the existence of a σ-polarized line at $\approx$15,867.8 cm^{-1}; (ii) the originating states of some of the σ lines. These points were easily resolved with the Enhancetron. The results are shown in Fig. 3. The upper trace shows the sum of eight scans, while the lower trace was obtained by four repetitions of scanning first with $T=12.6$°K while adding to the Enhancetron memory, then with $T=5.2$°K while subtracting. The upper trace confirms the existence of the 15 867.8-cm^{-1} σ line, while the lower trace shows that the 15 889.5-cm^{-1} and the 15 876.1-cm^{-1} σ lines must originate from the $M_s=0$ state, while the 15 881.2-cm^{-1} and the 15 872.1-cm^{-1} lines originate from the $M_s=\pm1$ states.

The energy-level diagram deduced from these measurements is shown in Fig. 4. Approximate relative intensities of the transitions are indicated (these have been corrected for population). The principal source of wave-number error in this diagram was in the visual determination of the peaks in the experimental traces. This can be seen to be $\approx\pm0.2$ cm^{-1}.

3. DISCUSSION

A. First-Order Theory: The Ham Effect

Ham's theory[4] refers to the effect of Jahn-Teller distortion on off-diagonal operators. A particular real representation (usually tetragonal) is forced on the system by the Jahn-Teller effect; and in a tetragonal representation the trigonal field, like the spin-orbit

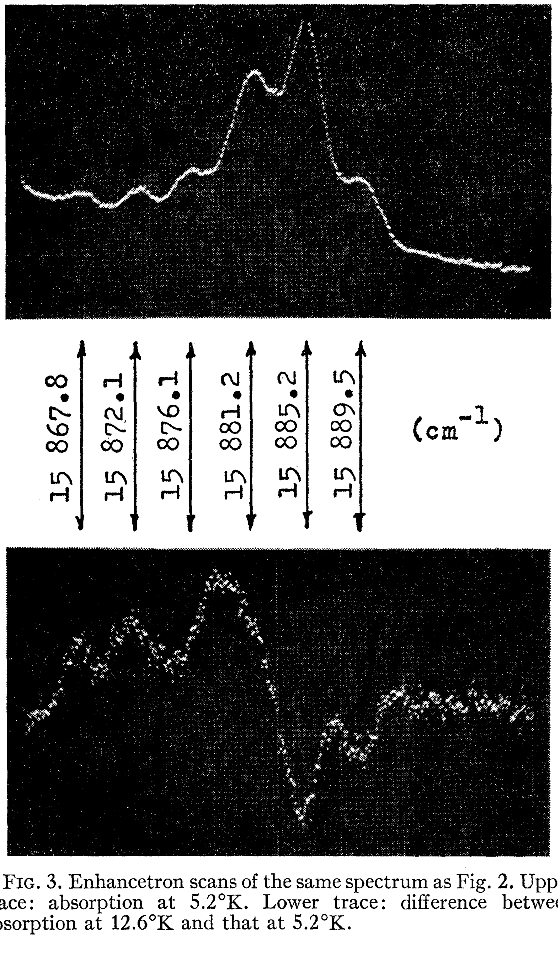

FIG. 3. Enhancetron scans of the same spectrum as Fig. 2. Upper trace: absorption at 5.2°K. Lower trace: difference between absorption at 12.6°K and that at 5.2°K.

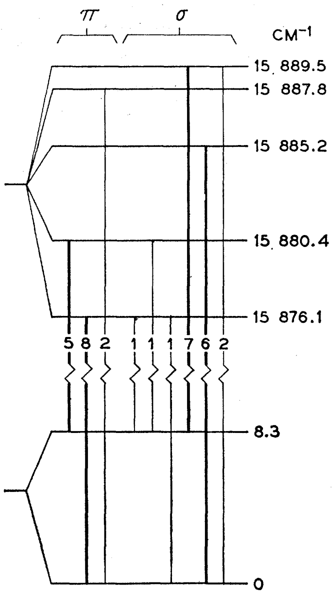

FIG. 4. Energy-level diagram for the $^3T_1(^3\hat{A})$ and $^3T_2$ (lowest vibronic) levels, deduced from Figs. 2 and 3. Relative intensities are indicated, corrected for population.

coupling and the orbital angular momentum, has no diagonal matrix elements. What we call the Ham effect is the partial or complete quenching of the first order splittings due to these off-diagonal operators. Ham also duscusses higher order effects which are not quenched; we will return to these later. As far as first-order effects are concerned, Ham predicts that a particular group of near-degenerate vibronic levels will show the same qualitative splitting pattern as they would have done in the absence of the Jahn-Teller effect; but the splittings will be reduced by a factor S, the overlap integral between the vibrational wave functions corresponding to different directions of Jahn-Teller distortion. For the lowest vibronic levels (i.e., those at the electronic origin of the band), in the harmonic approximation, Ham finds

$$S = \exp(-3\delta E/2\hbar\omega), \tag{1}$$

where δE is the Jahn-Teller energy (depression of the electronic origin below the unperturbed electronic level) and ω the frequency of ϵ_g vibrations.

The prediction of first order theory for the $^3T_2$ term of V^{3+} in a C_3 potential field is illustrated in Fig. 5(a). The trigonal splitting $v/2$ and the first order spin-orbit splitting $\zeta/4$ are reduced by the same factor S. So long as $\zeta/v \lesssim 1$, the strongest transitions from the $^3\hat{A}$ ground level will be those shown: they obey the selection rules

$$\hat{A} \rightarrow \hat{A}(\pi), \quad \hat{A} \rightarrow \hat{E}(\sigma), \quad \Delta M_s = 0. \tag{2}$$

Comparing with Fig. 4, we see that if we ignore the smaller splittings (less than 4 cm^{-1}) the σ and π selection rules are indeed obeyed by the stronger transitions[9]; and that the trigonal splitting has been reduced from 400 cm^{-1} (see Fig. 1) to about 9 cm^{-1}. Thus $S \approx 0.023$. As ζ is 155 cm^{-1}, $S\zeta/4$ is only 0.9 cm^{-1}, less than the line width (2 cm). Thus the spin-orbit coupling is quenched in first order and the remaining splittings must be second-order effects (see below). On the other hand, the trigonal field, while greatly reduced, is not completely quenched.

From the reduction factor of 0.023 we can deduce from Eq. (1) that $\delta E/\hbar\omega \doteqdot 2.5$; if $\hbar\omega \sim 200$ cm^{-1}, $\delta E \sim 500$ cm^{-1}. This is much less than the depression of the no-phonon line below the band maximum (≈ 1500 cm^{-1}), and probably indicates that totally symmetric (α_{1g}) vibrations are primarily responsible for the bandwidth.

B. Second-Order Theory

The main consequence of the Ham effect is that even when spin-orbit coupling is not strong enough to prevent Jahn-Teller distortion occurring, the qualitative appearance of the energy levels is the same as in the absence of the Jahn-Teller effect, but the first-order splittings are reduced. The same order of levels, with the same selection rules, will be seen in the presence of the Jahn-Teller effect, but the splittings will be reduced by the Ham effect.

In arriving at this conclusion, we have only considered matrix elements within the lowest group of degenerate vibronic levels of the Jahn-Teller distorted term. In a perturbation expansion these would be called first-order effects. We now turn to higher order effects, which involve matrix elements taking us out of the original vibronic level; we lump them together under

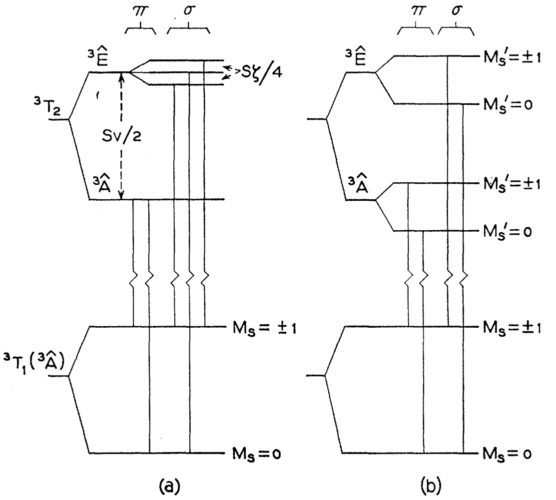

FIG. 5(a). Calculated energy-level diagram for the $^3T_2$ term in a trigonal field, neglecting second-order spin-orbit splittings. Here v is the trigonal field parameter; ζ, the spin-orbit coupling parameter; and S the overlap (reduction) parameter. Orbitally allowed transitions are shown. (b) Same as a, but including second-order spin-orbit splittings, and supposing the first-order spin-orbit splitting to be completely quenched. Transitions shown have $M_s = M_s'$.

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[9] Transitions violating (2) are weaker by a factor of about 5, as expected from the ratio ζ/v.

the heading "second-order effects." However small such matrix elements may be in the absence of the Jahn-Teller effect, if they are not reduced proportionately to the first-order matrix elements by the Ham effect they will ultimately become dominant. Ham shows that this limit corresponds to the static Jahn-Teller effect, in which the ordering of the levels is changed and the point symmetry lowered.

There are two classes of second-order effect. The first class arises from matrix elements connecting different terms and would be there even if there were no Jahn-Teller effect. The second class, which is the class discussed in detail by Ham, arises from matrix elements between vibronic levels of the term, and would not be there if there were no Jahn-Teller effect.

The first class is more or less unaffected in magnitude by the existence of Jahn-Teller distortion, so long as the terms involved are well separated relative to the Jahn-Teller energy (this is anyway a condition for the validity of a perturbation approach). This can be seen as follows. The electronic matrix elements have the form $\langle\Gamma\gamma|U|\Gamma'\gamma'\rangle$ where Γ is the term of interest, and Γ' another term connected by the operator U. Whatever the nuclear configuration associated with $|\Gamma\gamma\rangle$, there always exists an electronic state $|\Gamma'\gamma'\rangle$ associated with the same configuration. Thus, the matrix element between vibronic states is just the electronic matrix element, evaluated in that particular nuclear configuration. The energy denominator ΔE will be changed only an an amount of the order of the Jahn-Teller energy δE, which is *ex hypolhesi* small compared to the term separation. Thus, the order of magnitude of second-order terms diagonal in the ground vibronic level (i.e., of the form $|\langle\Gamma\gamma|U|\Gamma'\gamma'\rangle|^2/\Delta E$) is not altered by the Jahn-Teller effect. Off-diagonal second order terms are, of course, quenched.

The general formulas for the second class of second-order effects are complicated and are given by Ham. However, for a moderately strong or strong Jahn-Teller effect they simplify greatly; this is the only range in which one would expect them to be important relative to the first-order effects. In the limit of a strong Jahn-Teller effect, matrix elements connecting the two Jahn-Teller branches remain finite, giving contributions to the energy of the lowest level of the form $|\langle\Gamma\gamma|U|\Gamma\gamma'\rangle|^2/3\delta E$ ($3\delta E$ is the separation of the upper and lower branches). The criterion for the validity of this formula in the present case is $3\delta E \gg \zeta/4$, which certainly holds. Since δE, while large relative to $\hbar\omega$, may be small relative to term separations, the contributions of this type of second-order effect can be quite substantial.

The off-diagonal matrix elements (and the energy denominators) which appear in the two types of second-order effect are evaluated in a given, Jahn-Teller distorted, nuclear configuration, and in general will reflect the symmetry of this configuration. Thus, when the Ham effect is so strong that second-order effects are larger than first-order ones, the properties of the lowest vibronic level reflect the Jahn-Teller distortion: that is, we have a static Jahn-Teller effect. Note that in the lowest Jahn-Teller level the electronic state associated with a particular nuclear configuration is orbitally nondegenerate; a degenerate state would be unstable against further Jahn-Teller distortion. Thus, an orbital operator can produce no further splitting, and the only second order splittings we have to worry about are those due to spin-orbit coupling.

C. Second-Order Effects in Al_2O_3:V^{3+}

In the limit of the static Jahn-Teller effect the lowest electronic level of $^3T_2$ is an orbital singlet and can have no trigonal splitting. It is still a spin triplet, however, and can have a spin-orbit splitting in second order. The splitting arising from spin-orbit interaction with terms of d^2 (including the interaction with the upper Jahn-Teller branch, which was calculated by McClure) is

$$W(M_s'=\pm1)-W(M_s'=0)$$
$$=\sum_{M_s',M_s'',\Gamma,\gamma}(-1)^{M_s'}\frac{|\langle {}^3T_2M_s'0|V_{so}|S\Gamma M_s''\gamma\rangle|^2}{W(S\Gamma)-W({}^3T_2)}. \tag{3}$$

The spin index M_s is primed to indicate quantization along the axis of tetragonal distortion, rather than along the c axis of the crystal. $W(S\Gamma)$ is the energy of the level labeled $^{2S+1}\Gamma$.

It turns out that although the $^1T_2(t_2^2)$ and $^3A_2(e^2)$ terms independently make quite substantial contributions to (3), they nearly cancel, and the sum of second-order effects is quite small. Because of this accidental cancellation it is necessary to calculate the splitting to all orders in the spin-orbit coupling. This calculation has been made by Baltzer[10] who finds that for δE in in the range 250-1000 cm^{-1}, $W(\pm1)-W(0)$ lies in the range $+2$ to $+7$ cm^{-1}.[11] Of this, interaction with the upper Jahn-Teller branch only contributes about 1 cm^{-1}.[3]

This second-order spin-orbit splitting is shown superimposed on the first-order trigonal splitting in Fig. 5(b). The qualitative agreement of the energy level scheme with that observed (Fig. 4) is striking. The agreement is seen to be even better when it is remembered that the $\hat{E}$, $M_s'=\pm1$ level is fourfold degenerate in the present approximation. Coupling of the partially quenched orbital momentum (quantized along the c axis) to the spin will remove this degeneracy, the ex-

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[10] P. K. Baltzer (private communication).

[11] The fourth-order tetragonal parameter Dt is chosen to give the correct value of δE; the second-order parameter Ds is estimated from the point-charge model for a tetragonally distorted octahedron. The uncertainty in Ds is largely responsible for the uncertainty in the splitting.

pected splitting being of order $\zeta/180\sim 1\ \text{cm}^{-1}$.[12] Such a splitting is in fact observed.

It is important to remember in calculating the selection rules for transitions from the ground level that in the excited states spin is quantized along the direction of tetragonal distortion, while in the ground state it is quantized along the c axis (trigonal) of the crystal. If the tetragonal axis were at 54.7° to the c axis, no selection rule in M_s would be observed (except in the Zeeman effect). In fact, we notice that the system behaves rather as if spin were quantized along the c axis in both upper and lower states, transitions for which $M_s = M_s'$ being strongest. These are the transitions shown in Fig. 5(b). Presumably the axis of spin quantization is closer to the c-axis than our simple picture of a perfect octahedron immersed in an externally applied trigonal field would indicate.

D. The Anomalous Splitting of the $^3T_1 \rightarrow {}^3T_2$ Band

We have accounted for the main features of the electronic origin of the $^3T_2$ term by invoking the dynamic Jahn-Teller effect. Can such an effect also account for the fact that the splitting between the band maxima is small and of the wrong sign? On the basis of the Franck-Condon principle we would expect at least some trigonal splitting of the band. There will also be a Jahn-Teller splitting, which might be expected (by analogy with the case of an $A \rightarrow E$ transition[13]) to be roughly $(3\delta E\hbar\omega)^{1/2}\sim 600\ \text{cm}^{-1}$. This splitting would be the same for both polarizations (and therefore be unresolved, as the bandwidth is some $2500\ \text{cm}^{-1}$) if the Jahn-Teller distortion were indeed at 54.7° to the c axis. However, as in the case of the spin-splitting discussed earlier, deviation from this direction could lead to polarization. Thus, the splitting between the σ and π-polarized maxima could be partly due to the Jahn-Teller splitting.

This argument is rather implausible, however, as there is apprently a splitting of the same sign and roughly the same magnitude between the *centroids* of the σ- and π-polarized bands.[14] The first moment of a band is supposed to be independent of linear vibronic interactions[15] such as the Jahn-Teller interaction, and to depend solely on the mean crystal field. It is possible that the mean crystal field seen by the Jahn-Teller distorted ion is different from the static field because of nonlinear interactions between tetragonal and trigonal distortions. One source of such interaction is the mixing of terms by the tetragonal field; in particular, mixing of $^3T_1(te)$ into $^3T_2$ can have a large effect on the matrix elements of the trigonal field within $^3T_2$.

4. CONCLUSIONS

The lowest vibronic levels of the $^3T_2$ term of V^{3+} in Al_2O_3 are split in just the way predicted by Ham's theory for the case of an octahedral complex immersed in a crystal field of trigonal symmetry. The reduction in the first-order trigonal splitting by a factor of 45 is exceptionally clearcut evidence for the Ham effect, i.e., the partial quenching of an off-diagonal operator. While spin-orbit coupling is quenched to first order, higher order splittings are plainly visible, and are within the range predicted by the theory in the limif of a static Jahn-Teller effect. The splitting of the broad $^3T_1 \rightarrow {}^3T_2$ band, on the other hand, is not yet fully accounted for.

ACKNOWLEDGMENTS

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[12] In the static Jahn-Teller limit the symmetry is sufficiently low to remove all degeneracy, but only the fourfold degenerate level, which has both orbital and spin angular momentum, is split to first order in $S\zeta$.

[13] H. C. Longuet-Higgins, U. Öpik, M. H. L. Pryce, and R. A. Sack, Proc. Roy. Soc. (London) **A244**, 1 (1958), (see discussion of Fig. 4 of this reference); M. C. M. O'Brien, Proc. Phys. Soc. (London) **86**, 847 (1965).

[14] D. M. Dodd (unpublished spectra).

[15] M. Lax, J. Chem. Phys. **20**, 1752 (1952); D. E. McCumber, Phys. Rev. **135**, A1676 (1964).

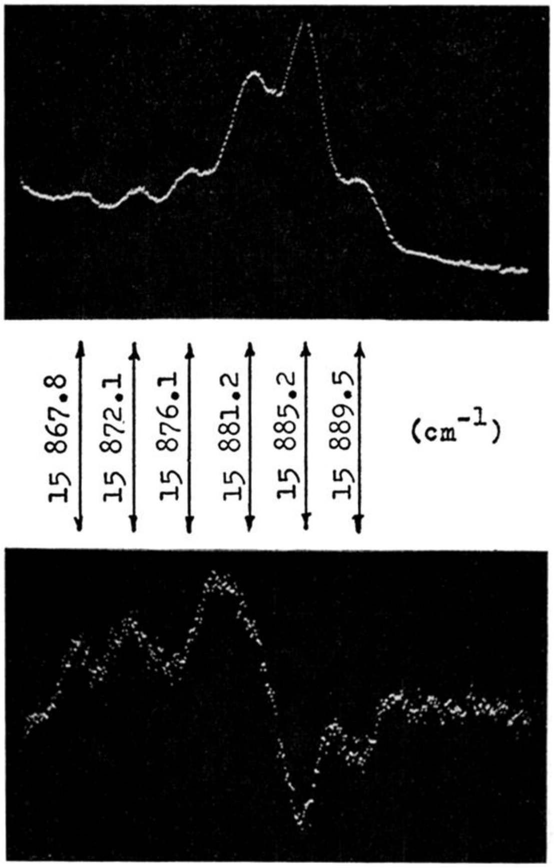

FIG. 3. Enhancetron scans of the same spectrum as Fig. 2. Upper trace: absorption at 5.2°K. Lower trace: difference between absorption at 12.6°K and that at 5.2°K.