Vibronically induced two-exciton bands in $KMnF_3$ and $RbMnF_3$

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Several two-exciton bands in the optical-absorption spectra of antiferromagnets $KMnF_3$ ($T_N \simeq 88$ K) and $RbMnF_3$ ($T_N \simeq 83$ K) are studied and their coupling energies, varying between 50 and 710 cm^{-1}, are determined. Also, the temperature dependence (10–300 K) of the oscillator strength, the line position E and the half-width at half maximum δ of two of these bands, $\alpha(A+A)$ and $\gamma(A+C)$, is measured. The oscillator strength of the α and γ bands decreases as the tempertaure increases, in agreement with an expression given by Fujiwara *et al.* For the parent A and C single-exciton bands, the oscillator strength increases up to T_N and then remains essentially constant above T_N. The line position follows an Einstein-type relation $E(T)=E(0)+A^*/[\exp(T^*/T)-1]$. For $KMnF_3$ ($RbMnF_3$) a single $T^*=569$ K (531 K) describes well the temperature dependence of the A, the α, and the γ bands, confirming that these vibronically induced transitions are promoted by a single phonon. The temperature dependence of δ for the α and γ bands in $KMnF_3$ also follows the Einstein-type relation. The above estimate of T^* agrees well with the known frequencies of a phonon in $KMnF_3$ and $RbMnF_3$.

I. INTRODUCTION

The excitation of two-exciton bands, upon the absorption of a single photon, in the optical absorption spectra of the Heisenberg antiferromagnets $KMnF_3$ and $RbMnF_3$, was first identified by Ferguson.[1] The magnon- or phonon-assisted single-exciton bands had been known from earlier studies in $KMnF_3$ and $RbMnF_3$ (Ref. 2) and MnF_2 (Ref. 3). Both $RbMnF_3$ and $KMnF_3$ have cubic structures with $T_N \simeq 83$ K for $RbMnF_3$ and $T_N \simeq 88$ K for $KMnF_3$,[3] although for $KMnF_3$ there is a slight distortion of the structure below T_N. MnF_2 has a tetragonal unit cell with $T_N \simeq 67$ K (Ref. 4), so that it is a good prototype for a uniaxial system. Stokowski *et al.*[5] studied the selection rules, polarization, and uniaxial stress behavior of the two-exciton bands in these systems and estimated the coupling energies for some of these bands. It is now understood that an odd-symmetry phonon is necessary to excite these bands whereas the coupling energy could come from the exciton-lattice interaction or from the exchange energy in the excited states.[5]

One of the characteristics of the two-exciton bands which distinguishes them from the exciton-magnon bands is the temperature dependence of their intensity or oscillator strength $I(T)$. According to Fujiwara *et al.*,[6] the intensity $I(T)$ of the two-exciton band should follow the equation

$$I(T)=\tfrac{1}{12}-\frac{\langle \vec{S}_j\cdot\vec{S}_l\rangle}{8S^2}+\frac{\langle \vec{S}_l\cdot\vec{Q}_j\cdot\vec{S}_l\rangle}{4S^2(2S-1)^2}\ , \tag{1}$$

where j and l are the nearest-neighbor magnetic ions involved in the excitation and Q is a symmetric tensor. For a Mn^{2+} ion with ground state $S=\frac{5}{2}$, Eq. (1) gives $I(0)/I(\infty)=3$. Thus the intensity of the two-exciton bands increases as the temperature is lowered through T_N, whereas for the exciton-magnon bands, the intensity decreases below T_N.[6] In a recent paper[7] we reported on the first detailed study of the temperature dependence of the lowest-energy two-exciton bands, α and β, in MnF_2 and $RbMnF_3$ and found complete agreement of the available data for the temperature range 10–300 K with Eq. (1). A somewhat similar variation of the α band in $BaMnF_4$ has been reported by Tsuboi and Kleeman.[8] In addition to the intensity we also measured the line positions $E(T)$ of the α and β bands in MnF_2 and $RbMnF_3$. By fitting this data to the equation

$$E(T)=E(0)+\frac{A^*}{\exp(T^*/T)-1}\ , \tag{2}$$

where A^* is a constant and T^* represents a phonon with frequency $\nu=k_BT^*/\hbar$, we were able to determine the frequency ν of the phonons associated with the lattice distortion accompanying the excitation of α and β bands in MnF_2 and $RbMnF_3$. These frequencies agreed with known phonons of odd symmetry in these materials.

In this work we have extended our studies of the exciton-magnon and the two-exciton bands to $KMnF_3$. Temperature dependence of the line positions $E(T)$, the oscillator strengths $I(T)$, and half widths $\delta(T)$ of several of these bands is reported for the temperature range of 10–300 K for the first time. We also report results on the higher-energy two-exciton bands in $RbMnF_3$ which were not investigated in our earlier work.[7] Results are compared with the temperature dependence predicted by Eqs. (1) and (2) and phonon frequencies and coupling energies are estimated. Details of these results follow.

II. EXPERIMENTAL PROCEDURES

Most of the experimental procedures used in this work are similar to the ones described in our recent paper. Measurements were carried out on a Cary 14 spectropho-

tometer in conjunction with a closed-cycle helium refrigerator for temperature control. The calibration of the Cary 14 was checked by using the known spectra of a standard sample of holmium oxide obtained from the National Bureau of Standards. Samples of several different thicknesses, varying between 0.2 and several mm, had to be used to accommodate different optical densities of various bands. The temperature resolution and stability was about 0.1 K, although the absolute accuracy is estimated to be only about ± 1 K.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Identification of bands

The unpolarized spectra of $KMnF_3$ at 300 and 10 K, in the wavelength range of 2000–6000 Å, are shown in Fig. 1. The spectra are similar to those reported for $RbMnF_3$ and MnF_2,[7] except for slight displacements of energies of the various bands and some details of the fine structure of some of those bands at temperatures below T_N. The bands labeled $A,B,C\ldots$ are magnon-exciton bands due to excitations from the Mn^{2+} ground state ${}^6A_{1g}$ to its quarted excited states ${}^4T_{1g}(I),{}^4T_{2g}(I),{}^4A_{1g}+{}^4E_g(I)\ldots$. Since these have been discussed in some detail in earlier papers,[1–8] we omit this discussion here. The two-exciton bands are labeled as $\alpha,\beta,\gamma\ldots$ in order of increasing energies and they respectively represent $A+A$, $A+B$, $A+C\ldots$ transitions. As noted in the Introduction and in Ref. 7, this labeling is facilitated by the observed *increase* in the intensity of the two-exciton bands on lowering the temperature through T_N vis-à-vis the magnon-exciton bands whose intensity *decreases* below T_N.

The observed spectra of $KMnF_3$, $RbMnF_3$, and MnF_2 in the higher-energy range are shown in Fig. 2. Again there are similarities in the spectra of the three antiferromagnets except for the slight shift in energies and slightly different oscillator strengths. The labeling $A+A$, $A+B$, etc. . . on top of the figure corresponds to the values for $KMnF_3$ only. It is noted that the positions of the two bands in $KMnF_3$ occur slightly on the lower-energy side of the positions predicted by $A+A$, $A+B$, etc. . . These differences are the coupling or binding energies of the various bands and they are all positive. We shall return to the discussion of these energies later on. Obvious from Fig. 2 is the fact that various two-exciton bands have considerably different oscillator strengths. This is probably due to different exciton-lattice couplings.[5]

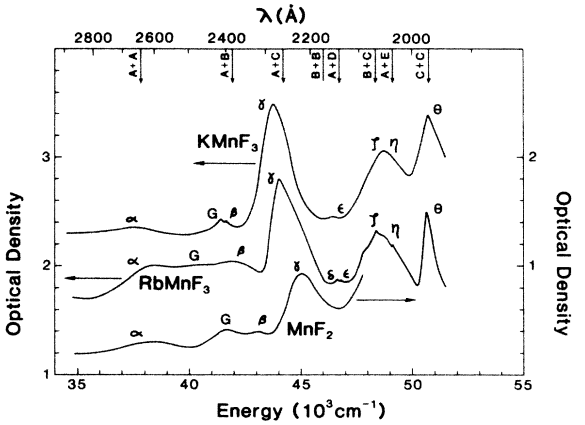

FIG. 2. Comparative plot of the absorption spectra of $KMnF_3$, $RbMnF_3$, and MnF_2 in the higher-energy range. Bands labeled with Greek letters are two-exciton bands. The labels $A+A$, $A+B$, etc. are the expected positions for $KMnF_3$.

B. Temperature dependence of the oscillator strength

The observed temperature variation of the oscillator strengths for the α and the γ band in $KMnF_3$ and the γ band in $RbMnF_3$ are shown in Fig. 3. The temperature dependence of the α band in MnF_2 and $RbMnF_3$ was reported in Ref. 7. The solid line is Eq. (1), obtained from

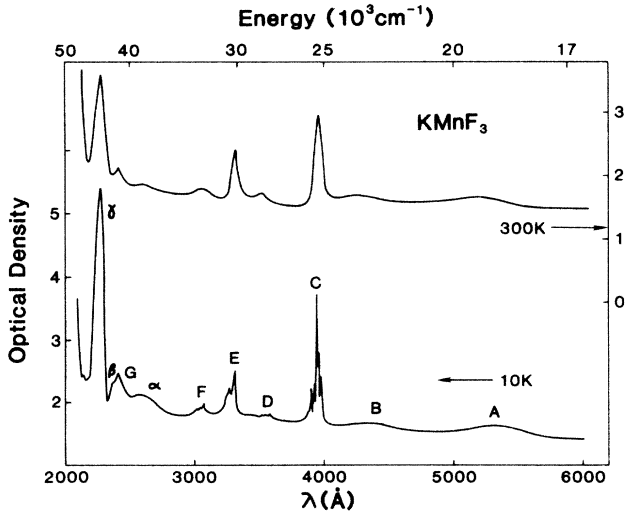

FIG. 1. Unpolarized optical absorption spectra of $KMnF_3$ at two temperatures. Labeling of the various bands is discussed in the text.

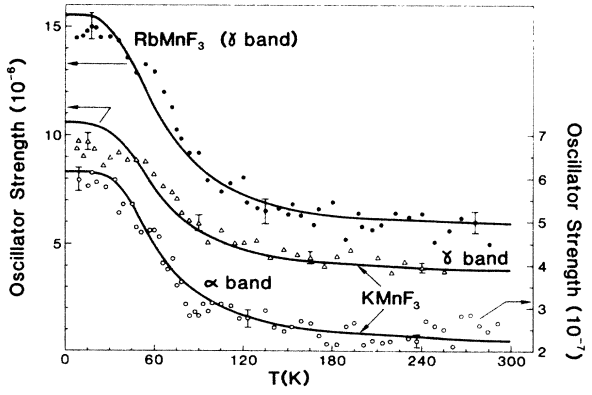

FIG. 3. Temperature variation of the oscillator strength for the α and γ bands in $KMnF_3$ and the γ band in $RbMnF_3$. Solid lines are theoretical fits to Eq. (1). Typical experimental errors are shown at a few selected temperatures.

Ref. 6 with a renormalization of temperatures according to $T_N \simeq 88$ K for $KMnF_3$. The theoretical curves are fitted at a single temperature so as to yield the best overall fit. The temperature dependence of the oscillator strengths for these agree very well with the predictions of Eq. (1), similar to our observations for the α band in MnF_2 and $RbMnF_3$.[7] It is noted that for the γ band, the sample thickness had to be reduced to 0.25 mm because of its higher optical density. The β band corresponding to $A+B$ bands is too weak for an accurate measurement of its oscillator strength and consequently no data on this band is presented here. The β band as well as the other two-exction bands of Fig. 2 on the higher-energy side, however, have temperatue dependences qualitatively similar to the data of Fig. 3. In any case, the detailed results presented here for the α and γ bands in $KMnF_3$, the γ band in $RbMnF_3$, and those on α band in $RbMnF_3$ and MnF_2 in our earlier work[7] have clearly established that Eq. (1) provides a correct description of the temperature dependence of the intensity of the two-exction bands, at least in the Mn^{2+} antiferromagnets.

For the A and the C band in $KMnF_3$, the temperature dependence of the oscillator strengths is given in Fig. 4. These bands are magnon-exciton bands which have been discussed in considerable detail by Fujiwara *et al.*[6] in the MnF_2 and $RbMnF_3$ system. The data presented on $KMnF_3$ is new. The solid lines are the calculated curves of Fujiwara *et al.*,[6] which have been normalized at one temperature to yield the best overall fit. Also the temperatures are scaled according to slightly different T_N for $KMnF_3$ compared to T_N for $RbMnF_3$ and MnF_2. For the A band, the curve is actually scaled from that calculated for MnF_2. The main points of the agreement with the theory are the decrease in the intensity below T_N with decreasing temperatures and near-constant values above T_N. For the C band, the data also show the peak near T_N predicted by the theory. The main departure from theory is at the lowest temperatures. The reasons for this disagreement are not understood.

Attempts were made to measure the oscillator strengths for the other two-exciton bands on the higher-energy side of the spectrum. However, because of either the weak intensity or the overlapping bands, accurate measurements as a function of temperature could not be made. The general behavior of a drop in intensity with increasing temperatures is, however, also observed for these bands.

C. Temperature dependence of the line positions

The variation in the line positions of the α band and the A band (as $A+A$) with temperature are shown in Fig. 5. For the A band, the line positions below T_N are not shown since fine structure (magnon side bands) below T_N appears which makes it difficult to determine accurately the position of the overall peak. The solid lines are fits to Eq. (2) with $T^*=569$ K. An excellent fit is evident in the whole temperature range with a difference in the line positions $E(A+A)-E(\alpha)=156$ cm^{-1}, which is temperature independent. The characteristic temperature $T^*=569$ K corresponds to $\nu=395$ cm^{-1}. In $KMnF_3$ there is a known transverse-mode phonon of odd symmetry with $\nu=395$ cm^{-1}.[9] This odd symmetry is essential to break the parity selection rule and make the otherwise forbidden electric-dipole transition allowed in the Mn^{2+} system. The important point of the fit in Fig. 5 is that we have independently determined the odd-symmetry phonon which is involved in the excitation of the A and the α bands. It should be noted that Eq. (2) is equivalent to

$$E(T)=E(0)\coth(h\nu/2k_BT)\ , \tag{3}$$

which is valid for the vibronically induced temperature dependence of the crystal-field parameters.[10] This provides a theoretical basis for our analysis.

Since the C band is presumably related to the γ band (see Fig. 2), we first show the temperature dependence of the C band before discussing the γ band. The tempera-

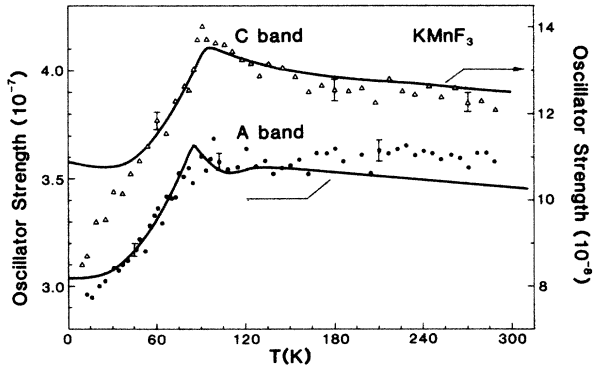

FIG. 4. Temperature dependence of the oscillator strengths for the A and C bands in $KMnF_3$. Solid lines are theoretical fits from Ref. 6. Error bars at selected temperatures are representative uncertainties.

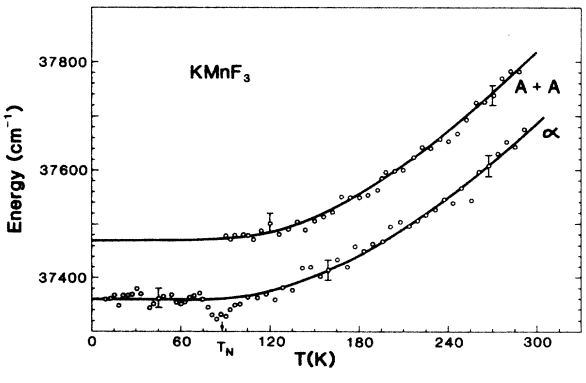

FIG. 5. Temperature variation of the line positions of the α and the A (as $A+A$) bands in $KMnF_3$ with representative uncertainties shown. Solid lines are fits to Eq. (2) with $A^*=990$ cm^{-1} (1877 cm^{-1}) for the A (α) band and $T^*=569$ K.

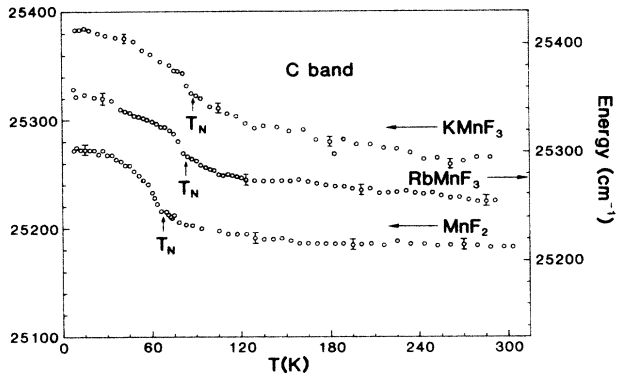

FIG. 6. Temperature dependence of the line positions of the C bands in $KMnF_3$, $RbMnF_3$, and MnF_2. Data for MnF_2 are shown for comparison purposes only. Positions of T_N for the three systems are noted.

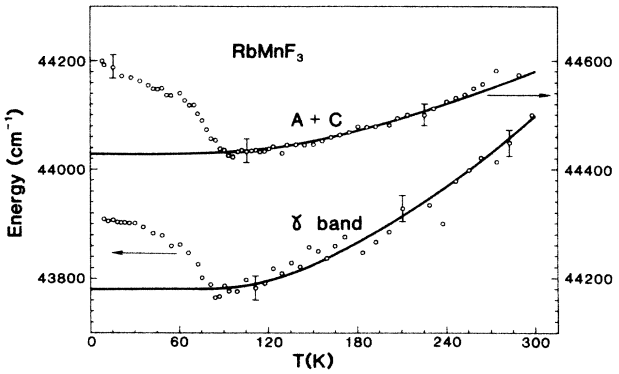

FIG. 8. Line positions of the γ band and the calculated $A+C$ positions (as in Fig. 7) for $RbMnF_3$. The solid line is due to Eq. (2) with $T^*=531$ K (see Ref. 7) and $A^*=731$ cm^{-1}. The values of E_0 are evident from the figure.

ture dependence of the line positions of the C band for $KMnF_3$, $RbMnF_3$, and MnF_2 is shown in Fig. 6, where the data for MnF_2 is from Ref. 11 and is given here primarily for comparison purposes. The variations for the three systems are essentially similar in that well above T_N there is no significant temperature dependence to the line positions and below T_N there is a blue shift. Such a blue shift of the lines below T_N has also been reported for MnO.[12] In MnF_2 it has been found that the blue shift is proportional to the sublattice magnetization below T_N.[11] Well above T_N the lack of temperature dependence to the line position is due to the fact that the quartet states $^4A_{1g}+{}^4E_g(I)$ which represent the C band are not perturbed by changes in the crystal field.[3,4] Thus the C band is ideal for investigating the effect of magnetic ordering since phonon effects are negligible.[11]

Next we consider the γ band ($A+C$). In Fig. 7 the observed temperature dependence of the line position of the γ band and the sum of the line positions of $A+C$ bands in $KMnF_3$ are shown. Again, data below T_N for $A+C$ is not shown because of the difficulty of accurately measuring the line position of the A band as mentioned earlier. The solid lines are fits to Eq. (2) with $T^*=569$ K, as for the α band, showing that the same phonon is involved in the excitation of the γ band. However, unlike the α band, there are deviations from the theoretical fit below T_N suggesting exchange energy in the excited state is perhaps contributing to the coupling energy of this two-exciton band. A similar result is observed in $RbMnF_3$ for the γ band, as shown in Fig. 8, in that the position is also shifted to higher energies below T_N. The value of $T^*=531$ K determined here is the same as determined from the fit to the α band in $RbMnF_3$ in our earlier work.[7] We will return to the question of coupling energies of the two-exciton transitions later on.

Among the other two-exciton bands (Fig. 2), band δ and ϵ are too weak for accurate measurements. Band θ could be followed up to about T_N and its line position is essentially temperature independent up to T_N. Band ζ and η are overlapping and consequently it is difficult to follow the variation of their changing line positions with temperature. So these data are not presented here.

D. Temperature dependence of the line widths

The variation of δ, the half widht at half maxima (HWHM), for band α and band γ in $KMnF_3$ is shown in

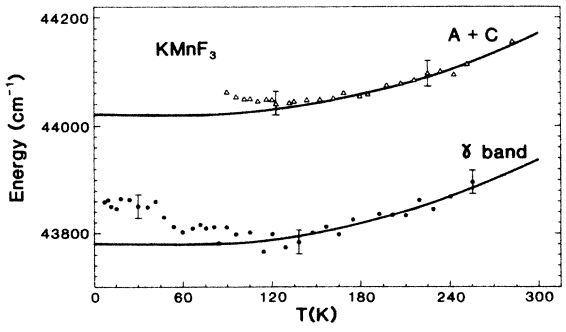

FIG. 7. Line positions of the γ band and the calculated $A+C$ positions (from the data for A and C bands) in $KMnF_3$. Solid lines represent Eq. (2) with $T^*=569$ K. $A^*=905$ cm^{-1} as for the α band. The values of E_0 are self evident.

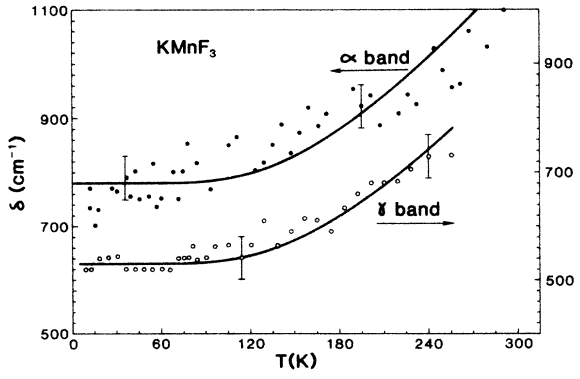

FIG. 9. Temperature dependence of HWHM δ for the α and γ bands in $KMnF_3$. Solid lines are fits to an equation of the form of Eq. (2) with $T^*=569$ K, and $A^*=2094$ cm^{-1} for the γ band.

TABLE I. Observed and expected line position of the various two-exciton bands in $KMnF_3$ and $RbMnF_3$ at 10 K. Asterisks denote line positions which were not clearly observed.

Band	Two-exciton bands Composition	Excited states	$KMnF_3$ Observed (cm^{-1})	$KMnF_3$ Expected (cm^{-1})	$KMnF_3$ Difference (cm^{-1})	$RbMnF_3$ Observed (cm^{-1})	$RbMnF_3$ Expected (cm^{-1})	$RbMnF_3$ Difference (cm^{-1})
α	$A+A$	$^4T_{1g}(I)+{}^4T_{1g}(I)$	37 658±35	37 814±10	156	38 311±35	38 488±10	177
β	$A+B$	$^4T_{1g}(I)+{}^4T_{2g}(I)$	41 628±35	41 948±20	320	42 272±35	42 418±20	146
γ	$A+C$	$^4T_{1g}(I)+{}^4A_{1g},{}^4E_g(I)$	43 857±50	44 254±10	397	43 910±50	44 620±10	710
δ	$B+B$	$^4T_{2g}(I)+{}^4T_{2g}(I)$	*	46 028±25	*	45 888±50	46 348±25	460
ϵ	$A+D$	$^4T_{1g}(I)+{}^4T_{2g}(II)$	46 664±50	46 758±20	94	46 937±50	47 192±20	255
ζ	$B+C$	$^4T_{2g}(I)+{}^4A_{1g},{}^4E_g(I)$	*	48 361±20	*	48 488±60	48 550±20	62
η	$A+E$	$^4T_{1g}(I)+{}^4E_g(II)$	48 739±75	49 126±10	387	49 264±75	49 534±20	270
θ	$C+C$	$^4A_{1g},{}^4E_g(I)+{}^4A_{1g},{}^4E_g(I)$	50 693±20	50 768±20	75	50 701±20	50 751±20	50

Fig. 9 for the temperature range of 10 K to about 300 K. For band α, there is considerable scatter in the data because the intensity of band α is somewhat lower than that of band γ and the question of proper base line has perhaps introduced an error which is difficult to estimate. In any case, δ increases with increasing temperatures which is expected for vibronically induced transitions. The solid lines are theoretical fits to Eq. (2) with $T^*=569$ K, as determined before from fits to the line positions. The fits are in reasonable agreement with the observations, confirming our contention that a phonon with $T^*=569$ K ($\nu=395$ cm^{-1}) is responsible for the excitation of α and γ, the two-exciton bands. We also note that there is no anomaly in the line width near T_N for the α and γ bands. This is in contrast to the anomaly observed for δ for the C and F band, the single-exciton bands.[11]

E. Coupling energies

In Table I we have listed the coupling energies of the various two-exciton bands determined in this work by subtracting the observed positions of the two-exciton bands from their expected positions. All coupling energies, listed as "Difference" in Table I, are positive as expected since a negative energy would imply that the two excitons are not bound and hence cannot be observed. We note this because in the earlier work of Stokowski *et al.*[5] negative coupling energies for some of the two-exciton transitions were implied. The magnitudes of the coupling energies for different two-exciton bands vary between 50 and 710 cm^{-1}. There appears to be no simple relationship between the coupling energies and the oscillator strengths of the bands. For example, the γ band is very intense and the coupling energy is also high (397 cm^{-1} in $KMnF_3$ and 710 cm^{-1} in $RbMnF_3$). But for the β band with a coupling energy of 320 cm^{-1} in $KMnF_3$ and 146 cm^{-1} in $RbMnF_3$, the oscillator strength is too low (see Figs. 1 and 2) for us to accurately study this band.

As noted in the Introduction, the coupling energy could come from the exciton-lattice coupling and from the exchange coupling in the excited states. From the temperature dependence of the position of the α band (Fig. 3 and Ref. 7 for $RbMnF_3$), it is clear that exchange interaction provides no significant contribution to the exciton-exciton coupling energy. However, for the γ band the deviations observed below T_N (Figs. 7 and 8) from the pure phonon description of Eq. (2) suggest partial contributions from exchange coupling. This contribution is about 50 cm^{-1} out of a total contribution of about 400 cm^{-1}. Thus our results suggest that the α band is a pure phonon-assisted band, whereas the γ band has some magnetic coupling, perhaps because of the parent C band.

IV. CONCLUDING REMARKS

Our final remarks concern the use of Eq. (2) [or, equivalently, Eq. (3)] for describing the temperature dependence of the line position of the two-exciton as well as the single-exciton bands in MnF_2, $RbMnF_3$, and $KMnF_3$. The fact that a single phonon provides such an excellent fit to the data leaves little doubt about the correctness of the physical description of the process. A similar excellent fit of the data to Eq. (2) of some phonon-assisted transitions in $CsNiBr_3$ have been recently reported.[13] It is noted that the same Einstein-type relation as Eq. (2) was used by Seehra *et al.*[14] to describe the observed temperature dependence of the static dielectric constants in the paramagnetic phase of MnO and MnF_2 and the frequencies of the phonons determined from this fit agreed exactly with the known frequency of an appropriate transverse optical phonon. Thus the result that a single optical phonon is responsible for the temperature dependence of the phonon-assisted optical transitions and of the dielectric constant is perhaps the most important finding of these studies. It should be quite interesting to see whether a similar description is valid in other systems.

[1]J. Ferguson, Aust. J. Chem. **21**, 307 (1968).
[2]J. Ferguson, W. J. Guggenheim, and Y. Tanabe, J. Phys. Soc. Jpn. **21**, 692 (1966).
[3]J. W. Stout, J. Chem. Phys. **31**, 709 (1959).
[4]D. M. Finlayson, I. S. Robertson, T. Smith, and R. W. H. Stevenson, Proc. Phys. Soc. London **76**, 355 (1960).
[5]S. E. Stokowski and D. D. Sell, Phys. Rev. B **3**, 208 (1971); S. E. Stokowski, D. D. Sell, and H. J. Guggenheim, *ibid.* **4**, 3141

(1971).
[6]T. Fujiwara, W. Gebhardt, K. Petanides, and Y. Tanabe, J. Phys. Soc. Jpn. **33**, 39 (1972).
[7]S. Darwish, S. Abumansoor, and M. S. Seehra, Phys. Rev. B **34**, 3198 (1986).
[8]T. Tsuboi and W. Kleemann, Phys. Rev. B **27**, 3762 (1983).
[9]J. D. Axe and G. D. Petitt, Phys. Rev. **157**, 435 (1966).
[10]W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. **139**, A1338 (1965); H. Klein, U. Scherz, M. Schulz, H. Setyonon, and K. Wisznewski, Z. Phys. B **28**, 149 (1977).
[11]M. S. Seehra and S. Abumansoor, Solid State Commun. **56**, 97 (1985).
[12]M. S. Seehra and R. D. Groves, J. Phys. C **16**, L411 (1983).
[13]T. Tsuboi and K. Iio, J. Phys. C **18**, 6059 (1985).
[14]M. S. Seehra, R. E. Helmick, and G. Srinivasan, J. Phys. C **19**, 1627 (1986); M. S. Seehra and R. E. Helmick, Phys. Rev. B **24**, 5098 (1981); J. Appl. Phys. **55**, 2330 (1984).