Thermal behavior of the two-exciton bands in MnF_2 and $RbMnF_3$

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(Received 8 April 1986)

Temperature dependence of the oscillator strength f and the line position E for several $d^n \rightarrow d^n$ absorption bands of Mn^{2+} in MnF_2 and $RbMnF_3$ is reported between 300 and 10 K. For the α and β two-exciton bands, the f values increase below T_N, whereas for the parent A and B bands, the f values decrease below T_N. For the α and β bands, the temperature dependence of f follows very well the prediction of Fujiwara *et al.* throughout the whole temperature range. The line positions of A, B, α, and β bands are fitted with the equation $E(T)=E(0)+A^*/[\exp(T^*/T)-1]$, with A^* and T^* being constants. It is shown that T^* corresponds to a characteristic frequency ν_t of odd-symmetry phonon which assists in the two-exciton absorption. For $RbMnF_3$, $\nu_t=369$ cm^{-1} for the A, B, α, and β bands, and for MnF_2, $\nu_t=295$ cm^{-1} for A and α bands and $\nu_t=158$ cm^{-1} for the B and β bands. These magnitudes agree with the known frequencies of some phonon modes in MnF_2 and $RbMnF_3$.

I. INTRODUCTION

MnF_2 and $RbMnF_3$ are well-known antiferromagnets with $T_N \simeq 67.3$ and 83.0 K, respectively. In these materials, absorption bands are observed in the visible-uv regions which are attributable to $d^n \rightarrow d^n$ transitions of Mn^{2+}. In the earlier studies of MnF_2 (Refs. 1–3) and $RbMnF_3$ (Ref. 4), the assignments of the major bands, viz. $A,B,C,\ldots$ were made as transitions from the sextet $^6A_{1g}$ ground state to the quartet $^4T_{1g}(I)$, $^4T_{2g}(I)$, $^4A_{1g}+{}^4E_g\ldots$ excited states. In these early studies, the temperature dependence of the spectra at a few selected temperatures between 20 and 300 K were also reported and the observed blue shifts of some of the bands below T_N were associated with the antiferromagnetic ordering. Later on, the observation of magnon sidebands for $T<T_N$ in a number of antiferromagnets generated a great deal of experimental and theoretical interest.[5] Among these excitations are the magnon-exciton (cold and hot) bands, the two-magnon transitions, and the two-exciton transitions. The temperature dependence of the magnon sidebands in MnF_2 and $RbMnF_3$ was computed by Fujiwara, Shinagawa, and Tanabe,[6] and a qualitative check on these predictions was provided by the experiments of Fujiwara *et al.*[7]

As the temperature is lowered below T_N, the integrated intensity (or the oscillator strength f) of the phonon-assisted, two-exciton bands is predicted to grow in intensity, whereas that of a magnon-exciton or a magnon-exciton-phonon band is predicted to decrease.[6–8] This prediction, however, has not yet been verified quantitatively in MnF_2 or $RbMnF_3$ in both the paramagnetic and antiferromagnetic regions. The transitions studied by Stokowski *et al.*[9] are the pure electronic transitions. These are the origins of the two-exciton bands. However, the predictions of Ref. 6 do not directly apply to these transitions. Besides, these studies[9] were limited to liquid-helium temperatures. In the work by Fujiwara *et al.*,[7] a direct comparison between theory and experiment for the two-exciton bands was not made, perhaps because the experiment indicated an increase in f above T_N, whereas the theory predicts a decrease in f with increasing temperatures. Also, only about a dozen data points in the range of 4 to 300 K were available.

In this paper, a detailed temperature dependence of the oscillator strengths f and the line positions E of the two-exciton bands (α and β), and the parent A and B bands, in MnF_2 and $RbMnF_3$, is presented. The data were taken in small temperature intervals from 10 to 300 K. The observed temperature dependence of f for the α band, in both MnF_2 and $RbMnF_3$, fits well the predicted behavior throughout the whole temperature range. For the β band, f values are considerably lower and so the data are limited to $T<130$ K. From the temperature dependence of the line positions of the A, α, B, and β bands, the frequencies of the phonons assisting in the two-exciton transitions are determined. Details of these results follow.

II. PERTINENT EXPERIMENTAL DETAILS

The optical absorption studies reported here were carried out on a Cary 14 spectrophotometer. Some details of the experimental procedures have been given in earlier publications.[10,11] A closed-cycle helium refrigerator (Air Products Displex System) in conjunction with a temperature controller (Air Products model APD-E) were used to obtain temperatures between 10 and 300 K. The temperature resolution and stability is 0.1 K, although the absolute accuracy is estimated to be about ± 1 K only. The single crystal of MnF_2 used here was grown by R. Fiegelson of Stanford University and loaned to us by A. S. Pavlovic. The single crystal of $RbMnF_3$ was grown at the Cornell Materials Science Center and obtained through D. W. Olson. The oscillator strengths were determined by retracing the bands on a tracing paper, cutting the curves, and accurately measuring the weight of the tracing paper. The weights could be reproduced to within 5%. For measuring the center positions of the bands, an average of three readings taken at a given temperature was con-

sidered. The thicknesses of the sample plates varied between 0.5 and 1.5 mm.

III. RESULTS AND ANALYSES

A. Band assignments

In Fig. 1, the unpolarized absorption spectra of MnF_2 at 300 and 10 K are shown. The bands have been labeled as A, B, C, D, E, F, α, G, and β in order of increasing energy. This labeling of α, G, and β bands is different from the earlier papers[1-3] but follows the convention used in the recent paper on $BaMnF_4$.[12] The integrated intensities of A, B, C, D, E, F, and G bands decrease or remain nearly constant between 300 and 10 K. On the other hand, the intensities of the α and β bands increase sharply on lowering the temperature. The bands α and β are the two-exciton bands, whereas the remaining bands are exciton-magnon or exciton-magnon-phonon transitions.[6,7,12] In a recent paper[11] we have reported on the temperature dependence of the exciton-magnon bands, C and F, in MnF_2. Here the emphasis is on the observed temperature behavior of the α and β bands, and the parent A and B bands in both MnF_2 and $RbMnF_3$. Qualitatively, the observed bands in $RbMnF_3$ are similar to those in MnF_2 shown in Fig. 1.

B. Temperature dependence of the oscillator strengths

In Fig. 2, the temperature dependence of the oscillator strength f for the α band in MnF_2 and $RbMnF_3$ is shown. Contrary to an earlier indication of an apparent increase in f above T_N,[7] no such increase is observed in our study. The dashed lines are computed curves for MnF_2 and $RbMnF_3$ and are based on the following expression for the intensity $I(T)$:

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

where j and l are the nearest-neighbor magnetic ions and $\overleftrightarrow{\mathbf{Q}}$ is a symmetric tensor.[7] For Mn^{2+}, $S=\frac{5}{2}$ and Eq. (1) gives $I(0)/I(\infty)=3$. From Fig. 2, it is clear that the observed temperature dependence of f for the α band in MnF_2 and $RbMnF_3$ follows closely the predicted behavior

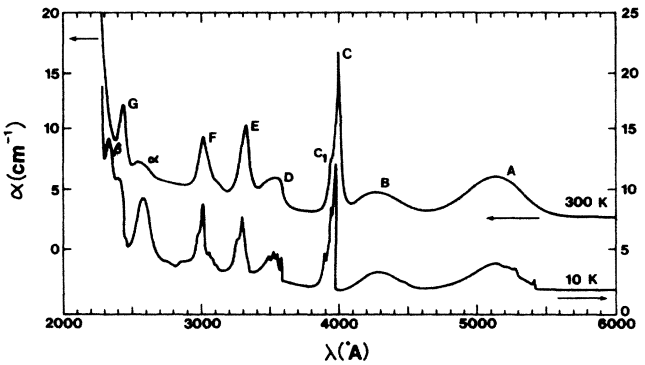

FIG. 1. Absorption coefficient α against wavelength λ for MnF_2 at 300 and 10 K. Bands A, B, α, and β are discussed at length in text.

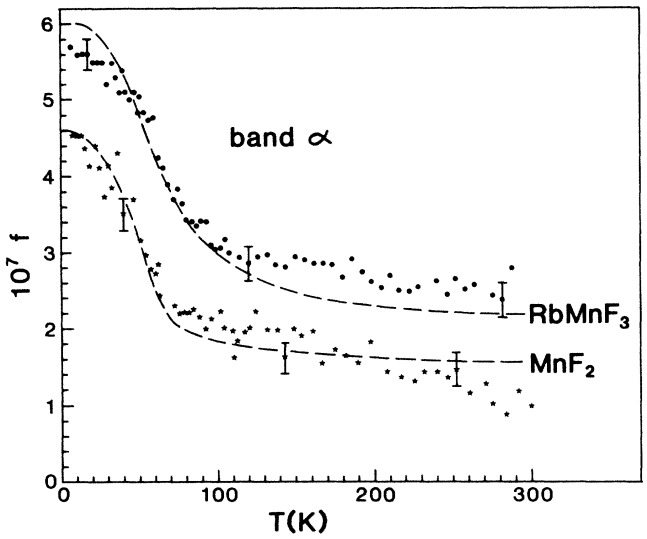

FIG. 2. Temperature dependence of the oscillator strength f for band α in MnF_2 and $RbMnF_3$. The dashed lines are the theoretical curves from Ref. 7.

for a two-exciton band.[7] (The computed curves in Fig. 2 are normalized at one temperature to yield the best overall fit with the data.) Now, the A band is due to the transition to the ${}^4T_{1g}(I)$ state. So the α band corresponds to the transition to ${}^4T_{1g}(I)+{}^4T_{1g}(I)$ for the two nearest neighbors. In Table I, it is seen that the energy of the α band is nearly twice that of the A band, as expected.

For the β band in MnF_2 and $RbMnF_3$, the oscillator strength f also decreases as the temperature increases, in a manner similar to the α band. However, as seen in Fig. 1, the f values for the β band are difficult to determine accurately first because of the base line problem (see Fig. 1), and second because of the much smaller intensity of the β band. The position of the β band, however, can be followed to about 130 K. This is discussed next.

C. Temperature dependence of the line positions

The temperature dependence of the line positions for the A and the α band is shown in Fig. 3 for MnF_2 and in Fig. 4 for $RbMnF_3$. Below about 100 K the center of the A band is difficult to determine accurately because of the appearing fine structure and resulting distortions in the band, and so no data below this temperature are shown. However, it is noted that there is a general tendency towards blue shifts below T_N, as clearly documented and discussed for the C and F bands.[11]

Since band A is believed to be a phonon-assisted transition, we have fitted the position of the band, $E(T)$, to an Einstein-type function

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

where A^* is a constant and T^* is the characteristic temperature of a phonon with frequency ν_t ($k_BT^*=h\nu_t$, where k_B and h are, respectively, the Boltzmann and Planck constants). The dashed curves in Fig. 3 and Fig. 4 are fits to Eq. (2) with parameters given in Table I. Excel-

TABLE I. Parameters of Eq. (2), evaluated from the fit to the data for the A, B, α, and β bands in $RbMnF_3$ and MnF_2.

	Band	Excited states	$E(0)$ (cm^{-1})	A^* (cm^{-1})	T^* (K)	ν_t (cm^{-1})
$RbMnF_3$	A	$^4T_{1g}(I)$	19150	925	531	369
	B	$^4T_{2g}(I)$	23115	1144	531	369
	α	$^4T_{1g}(I)+{}^4T_{1g}(I)$	38295	1850	531	369
	β	$^4T_{1g}(I)+{}^4T_{2g}(I)$	42257	4876	531	369
MnF_2	A	$^4T_{1g}(I)$	19418	432	425	295
	B	$^4T_{2g}(I)$	23384	161	227	158
	α	$^4T_{1g}(I)+{}^4T_{1g}(I)$	38970	576	425	295
	β	$^4T_{1g}(I)+{}^4T_{2g}(I)$	43080	1239	227	158

lent fits to Eq. (2) are obtained with a unique magnitude of ν_t for both the A and α bands. To our knowledge, such an explanation of the shift of the line position of a two-exciton band has not been forwarded before.

For the B and β bands, a procedure similar to the above is followed and the data and the fits to Eq. (2) are given in Fig. 5 for MnF_2 and in Fig. 6 for $RbMnF_3$. Below T_N, the B band undergoes a blue shift similar to the observations for the C and F bands.[11] The fit to Eq. (2) therefore considers the data only for $T > 100$ K, where the magnetic contributions are negligible. For the β band, no data above 135 K are shown since this band essentially disappears above this temperature. The parameters of the fits to Eq. (2) for the B and β bands are also given in Table I.

IV. DISCUSSION

From the magnitudes of the parameters in Table I, it is clear that in $RbMnF_3$, only a single phonon with frequency $\nu_t = 369$ cm^{-1} is involved in the excitation of A, B, α, and β bands. On the other hand, in MnF_2, two phonons are involved; one with $\nu_t = 295$ cm^{-1} for the excitation of A and α bands and the other with $\nu_t = 159$ cm^{-1} for the excitation of B and β bands. This difference between the two systems is perhaps the result of different symmetry around Mn^{2+} in MnF_2 and $RbMnF_3$. For the α band in $RbMnF_3$, the magnitude of A^* and $E(0)$ are twice that for the A band. For the α band in MnF_2, although $E(0)$ is nearly twice that for the A band, the magnitude of A^* for the α band is not twice that of the A band. Similarly for the β band, although the energy $E(0)$ is nearly equal to the sum of the energies of the A and B bands as expected, no relationship is evident between the magnitudes of A^*. By varying A^* and T^* in Eq. (2) and considering fits to the data, it is estimated that the magnitudes of A^* and T^* are reliable to within 5%.

There is a valid justification for using Eq. (2) to describe the temperature dependence of the line positions. The reasoning is as follows. In general, the temperature dependence of a crystalline parameter such as E has two contributions: a static or implicit variation due to thermal changes in the lattice constant and a dynamic (vibrational) or explicit variation due to phonons.[13] If only a single phonon is involved, then the explicit variation has exactly the form of Eq. (2).[13] The implicit temperature dependence, on the other hand, varies with the lattice constant R as R^n, where the magnitude and sign of n depends upon the crystalline symmetry.[13] An estimation of the relative magnitudes of the two contributions is not always straightforward. Also, from the two parameter fits

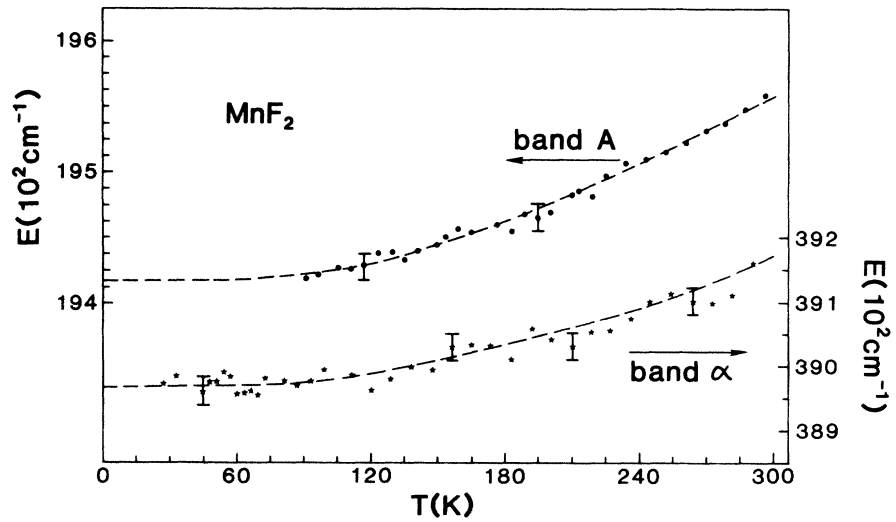

FIG. 3. Temperature dependence of the line positions E for the A and α bands in MnF_2. The dashed lines are fits to Eq. (2), with parameters given in Table I.

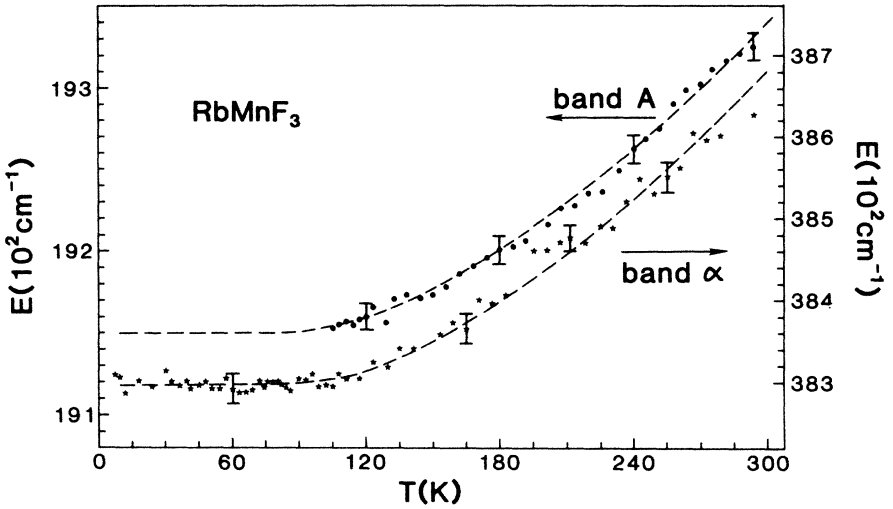

FIG. 4. Temperature variation of the line positions E for the A and α bands in $RbMnF_3$. The dashed lines are fits to Eq. (2), with parameters given in Table I.

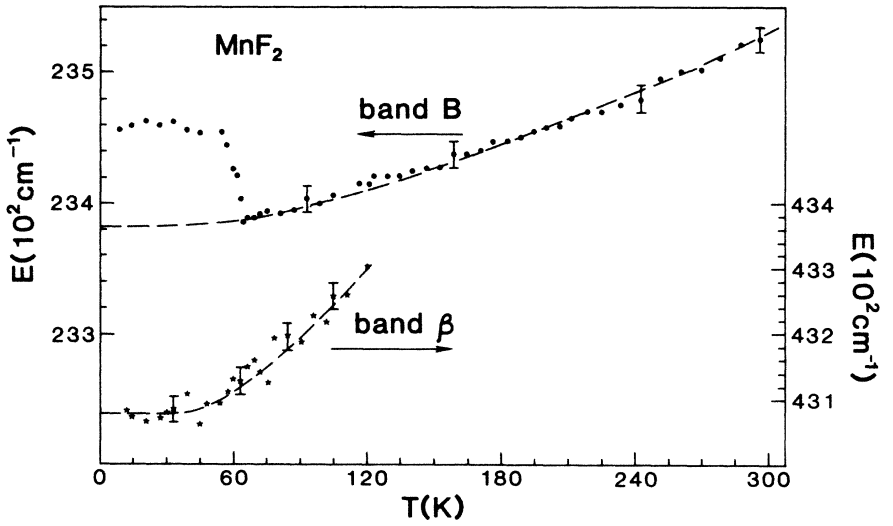

FIG. 5. Thermal behavior of the positions E of the B and β bands in MnF_2. Dashed lines are fits to Eq. (2). See Table I for the fitting parameters. The blue shift below 90 K for the B band is ignored in fitting to Eq. (2). See text for discussion.

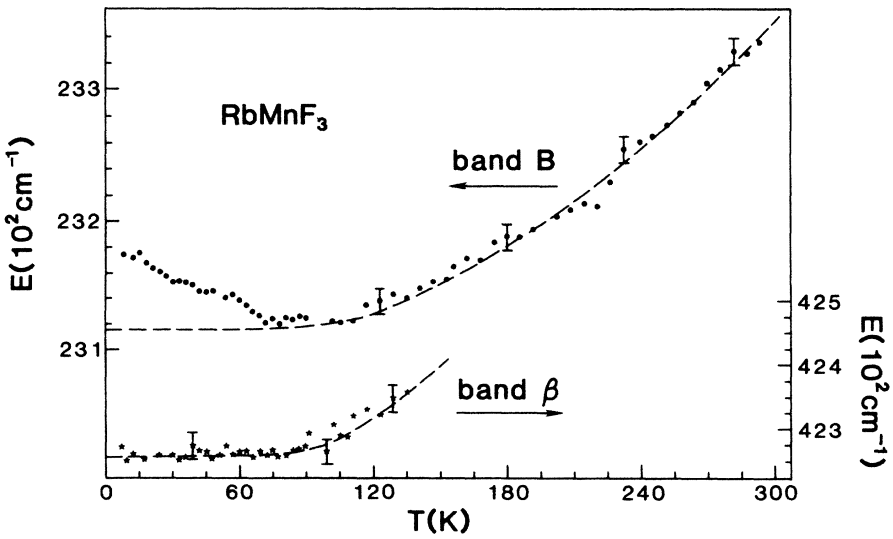

FIG. 6. Same as Fig. 5 except that the data are for $RbMnF_3$.

of the data to Eq. (2) alone, one should be careful to deduce that the implicit temperature dependence is absent. However, in the present case, there are several reasons which suggest that the implicit temperature dependence is not important for two-exciton bands in MnF_2 and $RbMnF_3$. First, there are anomalies in the lattice parameters of MnF_2 and $RbMnF_3$ near T_N due to magnetic ordering,[14] whereas no anomalies are observed in the line positions of the α and β bands. This suggests the absence of a contribution of the type $E \simeq R^n$. Second, since an odd-symmetry phonon is essential for the excitation of the A, B, α, and β bands, it follows that the vibrational or explicit temperature dependence should dominate. And third, the frequencies determined from the fit are close to the known frequencies of some phonons, as discussed below.

In considering the various phonon modes of MnF_2, it is found that two modes, $A_{2u}(\Gamma_1^-)$ and $E_u^1(\Gamma_5^+)$, have the appropriate frequencies[15] of 295 and 158 cm^{-1}, determined in this work from fits to Eq. (2). These modes also have the appropriate odd symmetry which is essential to make the electric dipole transition allowable in the Mn^{2+} system. Similarly, for $RbMnF_3$, there is a phonon of E_u symmetry[16] with $\nu_t = 369$ cm^{-1}, in agreement with the magnitude determined in this work (Table I). The use of Eq. (2) to determine the appropriate phonon modes and to describe the temperature dependence of the line positions is an important result of this work.

From Figs. 3–6, it is clear that for the two-exciton bands, there is no noticeable shift of the line positions at T_N, whereas the line positions of the exciton-magnon bands clearly mark the onset of magnetic ordering. This is consistent with the physical picture in which a magnon is involved in the exciton-magnon transition and no magnon is needed for the two-exciton transition.[17] This along with the differences in the temperature behavior of their oscillator strengths provide strong distinctions between the two-exciton and the exciton-magnon bands.

We have also measured the oscillator strengths of the A and B bands as a function of temperature. Between 10 K and T_N, the oscillator strengths for these bands in MnF_2 and $RbMnF_3$ increase monotonically, and above T_N, they are weekly temperature dependent. These observations are similar to the results reported by Fujiwara *et al.*[7] Although, the temperature dependence of the hot and cold sidebands has been treated theoretically,[6] the temperature dependence of the area under the whole band which includes contributions from the phonons is difficult to determine. Consequently, no discussion on the oscillator strengths of the A and B bands has been given in this work.

In summary, it has been shown that in MnF_2 and $RbMnF_3$ the temperature dependence of the oscillator strength of the two-exciton bands is described well by Eq. (1) and their line position by Eq. (2). The frequencies of the phonons determined from this work agree with the known frequencies of some phonons in these systems.

ACKNOWLEDGMENTS

One of us (M.S.S.) wishes to thank A. S. Povlovic and D. W. Olson for the loan of the samples used in this study. This research was supported in part by the National Science Foundation, Grant No. DMR81-06620.

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