PHYSICAL REVIEW B VOLUME 27, NUMBER 1 1 JANUARY 1983

Isotope effects in the multiphonon relaxation of hydrated and deuterated cesium chloromanganate ($CsMnCl_3\cdot 2H_2O,\cdot 2D_2O$)

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(Received 19 July 1982; revised manuscript received 7 September 1982)

The electronic transition between the $^4T_1$ and $^6A_1$ states of the Mn^{2+} ion in $CsMnCl_3\cdot 2H_2O$ has been observed to be weak compared to the same transition in other hosts, due to vibrational quenching. We have observed fluorescence and infrared-absorption spectra of the deuterated compound $CsMnCl_3\cdot 2D_2O$ and report little change in the phonon sideband associated with the pure electronic transition, but observe a 15-fold increase in the lifetime of the excited state, along with an increase in the $^4T_1$ luminescence intensity. Infrared spectra reveal an intense band of high-frequency phonons which exhibits a large shift in energy with isotopic substitution. We show that these data are consistent with the theory of multiphonon transitions recently presented by Huang and Gu.

I. INTRODUCTION

In an earlier paper[1] we reported on the optical properties of the $^4T_1$ to $^6A_1$ transition of Mn^{2+} in the quasi-one-dimensional antiferromagnetic material $CsMnCl_3\cdot 2H_2O$ (CMC-H).[2,3] In this earlier work we showed that, consistent with theories of energy transport in nearly-one-dimensional systems, the optical excitations in CMC-H are localized and energy migration at low temperature is very slow.[4] We observed, however, that the lifetime of the $^4T_1$ state is only 0.58 ms, compared to typical lifetimes in other hosts of from 1 to 10 ms. The localization of the excitation rules out quenching due to migration to traps, and we speculated that the multiphonon decay due to phonons associated with the O-H stretching modes of the waters of hydration caused the reduction in the lifetime.

We have since carried out fluorescence and infrared-absorption experiments on deuterated cesium chloromanganate (CMC-D) and have observed the following apparently contradictory changes. The phonon sideband of the pure electronic transition was little affected by the isotopic substitution but the lifetime of the $^4T_1$ state increased by a factor of 15. The infrared spectrum of CMC-D shows that the intense band observed at 3300 cm^{-1} in CMC-H (Ref. 5) shifts to 2450 cm^{-1} with isotopic substitution.

The results of the fluorescence experiments cannot be made consistent with those predicted by the most widely used model of multiphonon processes in solids, the single-configuration-coordinate (SCC) model.[6-9] We have successfully analyzed the CMC-H and CMC-D systems using the recent theory of multiphonon decay of Huang and Gu.[10]

The remainder of the paper is organized as follows. The experimental details and results are presented in Sec. II. In Sec. III we analyze the phonon sidebands using the SCC model and show that this model cannot account for the change in the lifetime of the deuterated system and the observed asymmetry in the phonon sideband. We present in Sec. IV an analysis of the data using the theory of Huang and Gu and show this model gives excellent agreement. Section V is devoted to discussion of the results of the analysis and concluding remarks.

II. EXPERIMENTAL METHODS AND RESULTS

CMC-D samples were grown by evaporation from supersaturated solutions of heavy water, cesium chloride, and magnesium chloride of 99% or 99.9% purity. Some contamination of the samples by water occurred, as no great effort was made to dehydrate the solutes. Single crystals of good optical quality and moderate size were obtained. Additional details on the crystal-growing procedures appear in Ref. 1.

The $^4T_1$ fluorescence was excited by pumping the phonon sideband at 514.5 nm with an argon-ion laser or the zero-phonon transition resonantly with a pulsed nitrogen-pumped dye laser, the latter used to make the lifetime measurements. The fluorescence spectra were resolved by a Spex 1-m double spectrometer and detected with a cooled RCA C31034A photomultiplier. All fluorescence measurements were performed with the samples immersed in superfluid liquid helium at a temperature of 1.6 K.

The fluorescence emission spectra of CMC-H and CMC-D are shown in Fig. 1. The fluorescence de-

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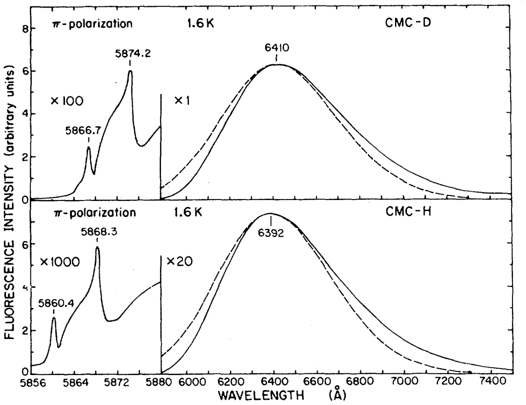

FIG. 1. Fluorescence spectra of zero-phonon $^4T_1$-$^6A_1$ transitions and associated magnon and phonon sidebands in CMC-D and CMC-H. Dashed line is fit to phonon sideband using SCC model. The vertical scales for CMC-D and CMC-H are different.

cays from the $^4T_1$ state in the two hosts are shown in Fig. 2. Isotopic substitution causes several changes in the fluorescence spectrum. The fluorescence intensity is greater in CMC-D. The position of the zero-phonon line in CMC-D shifts to the red by 18 cm^{-1} relative to that in CMC-H. The peak of the phonon sideband in CMC-D occurs at 1465 cm^{-1} from the zero-phonon transition, compared to 1418 cm^{-1} in CMC-H. Finally, the lifetime of the fluorescence is 9.2 ms in CMC-D and 0.58 ms in CMC-H.

Room-temperature infrared spectra were taken on both the hydrated and deuterated samples using a Perkin-Elmer model 1310 infrared spectrophotometer. Samples with a thickness of approximately 1 mm were used. He gas was directed over the samples to prevent oxidation. The spectrum of the hydrated samples revealed a broad intense band centered at 3300 cm^{-1} and a weaker band at 1600 cm^{-1}, in agreement with the observations of Singh *et al.*[5] The CMC-D sample showed a residual peak at 3300 cm^{-1} due to contamination, along with a new strong broad feature at 2450 cm^{-1}. Several sharp weak features were seen at 1600 cm^{-1} and below. The ratio of the frequencies of the intense features is 0.74, as one would expect for vibrations associated with O-H and O-D stretching modes.

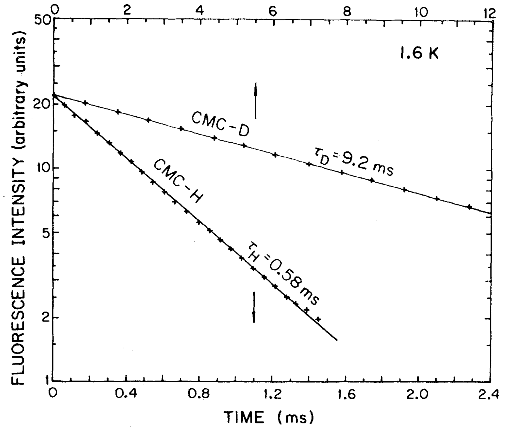

FIG. 2. Fluorescence decay of CMC-H and CMC-D.

III. ANALYSIS USING THE SCC MODEL

The SCC theory of multiphonon-assisted transitions has been applied to the analysis of the absorption bands of a great number of insulators including the antiferromagnetic materials MnF_2 (Ref. 11) and $RbMnF_3$ (Ref. 12). It has been shown, for example, that in the latter Mn^{2+} compounds up to five phonons of average frequency $\hbar\bar{\omega}_s$ assist in the formation of the strong phonon sidebands which are observed. In these analyses by Gebhardt and coworkers, it is required that the excited state in question by relatively well localized, i.e., that no strong energy transfer or dispersion predominate in this state. This condition has been shown to be satisfied in both CMC-H and CMC-D, owing principally to its low dimensionality.[1]

In the SCC model the spectral shape of the phonon-assisted emission may be written as

$$I(E=W_{ji}-\hbar\bar{\omega})=|M_{ji}|^2e^{-S}[\delta(\bar{\omega})+\sigma_1(\bar{\omega})+\cdots+\sigma_n(\bar{\omega})/n!] \ . \quad (1)$$

In Eq. (1), M_{ji} is the appropriate dipole matrix element coupling the ground state $|i\rangle$ and excited state $|j\rangle$, W_{jk} is the energy of the zero-phonon transition, and $\hbar\bar{\omega}$ is the energy of emission relative to the zero-phonon line. The power S is known as the Huang-Rhys factor and serves as a measure of the electron-phonon coupling strength. $\delta(\bar{\omega})$ is the zero-phonon-line intensity, and $\sigma_n(\bar{\omega})$ is the intensity contribution of the nth-order phonon mode in the phonon progression.

At low temperatures S may be considered constant, so that the intensity of the zero-phonon line can be written as

$$I(W_{ij})=|M_{ji}|^2e^{-S} \quad (2)$$

$$=I_0e^{-S} \ , \quad (3)$$

where I_0 is the integrated intensity of the transition. The Huang-Rhys factor is then given by the natural logarithm of the ratio of the integrated intensity of the transition to that of the zero-phonon line.

Applying the SCC model to our experimental data leads to Huang-Rhys factors of $S_{\mathrm{H}}=9.5$ for CMC-H and $S_{\mathrm{D}}=9.7$ for CMC-D. Since the S factor is in effect a measure of the lattice relaxation energy, the above results indicate that no dramatic changes in the electron-phonon coupling occur because of isotopic substitution.

We may also use the SCC model to calculate the shape of the phonon sideband. In the strong-coupling limit the intensity as a function of energy has the form[9]

$$I(E)=\frac{|M_{ij}|^2}{[2\pi S(\hbar\bar{\omega}_S)^2]^{1/2}}\exp\left[-\frac{(E-\bar{E})^2}{2S(\hbar\bar{\omega}_S)^2}\right] . \tag{4}$$

The profile of the sideband is thus predicted to be a Gaussian centered at

$$\bar{E}=W_{ji}-S(\hbar\bar{\omega}_S) . \tag{5}$$

In Eqs. (4) and (5), $\hbar\bar{\omega}_S$ represents the average energy of the phonons involved in the sideband formation. The width (full width at half maximum) of the profile is

$$\Delta E=2[2\ln 2S(\hbar\bar{\omega}_S)^2]^{1/2} . \tag{6}$$

The dashed lines in Fig. 1 are the phonon sideband profiles calculated using the SCC model, which can be seen to give an adequate fit to the observed sidebands. The model gives a value of the average energy of the phonons involved in the sideband as $(\hbar\bar{\omega}_S)_{\mathrm{H}}=149$ cm^{-1} and $(\hbar\bar{\omega}_S)_{\mathrm{D}}=150$ cm^{-1}, with a predicted width of $\Delta E=1100$ cm^{-1}, compared to an observed width of 1150 cm^{-1}.

We note that the theoretical model used in these fits cannot account for the pronounced asymmetry towards the red observed in the sidebands. Asymmetries of this type in other materials have been ascribed to phonon replication of the magnon sidebands.[13] In such cases the magnon sidebands were, because of selection rules, much stronger than the zero-phonon transitions. As can be seen from the expanded plot of the zero-phonon transitions and associated magnon sidebands in Fig. 1, this is not the case in either CMC-H or CMC-D. We shall see below the source of this asymmetry can be found in the influence of high-energy phonon groups.

The SCC model does give us a qualitative if not exact description of events leading to the formation of the sidebands in CMC. As in other Mn^{2+} systems, low-frequency phonons roughly assignable to the acoustic branches are implicated in the sideband formation. We can conclude, faithful to our physical intuition, that bulk-phonon properties do not appear to be modified by deuteration of the CMC lattice.

However, this result is inconsistent with the increase in lifetime by more than an order of magnitude observed in CMC-D. According to the SCC model, if the phonon sideband is unchanged by isotopic substitution, there should be little change in the multiphonon contribution to the decay of the excited state. Clearly one must take into account the change in frequency of the water stretch modes on isotropic substitution to account for the change in lifetime. The model developed by Huang and Gu allows one to do just that, as we show in the following section.

IV. ANALYSIS USING THE MULTI-FREQUENCY MODEL OF HUANG AND GU

Huang and Gu have recently presented a theory of multiphonon transitions based on the idea that the phonons active in phonon-assisted relaxation in solids can be arranged in groups with an effective frequency of $\hbar\omega_t$ and with a corresponding coupling to the excitation given by S_t.[10] Using a statistical thermodynamic formalism they found that the rate of multiphonon decay at an energy E_{ij} is proportional to

$$\frac{1/\sqrt{2\pi}\,\exp\left[\mu E_{ij}+\sum_t S_t e^{-\mu\hbar\omega_t}-S\right]}{\left[\sum_t S_t(\hbar\omega_t)^2 e^{-\mu\hbar\omega_t}\right]^{1/2}} , \tag{7}$$

where μ corresponds to an inverse temperature in the thermodynamic formalism and is determined by the equation

$$E_{ij}=\sum_t S_t\hbar\omega_t e^{-\mu\hbar\omega_t} . \tag{8}$$

The S in Eq. (7) is the same Huang-Rhys factor defined earlier, and is just the sum over all the groups t of S_t. The number of phonon groups considered to be active is totally arbitrary in the theory, so that this model forms an intermediate link between the cumbersome and difficult general theory of multiphonon relaxation[9] and the over-simplified picture of the SCC model.

For the phonon-assisted radiative transitions which make up the phonon sideband, E_{ij} in Eqs. (7) and (8) is the energy shift from the zero-phonon line. For multiphonon nonradiative decay from the excited state, E_{ij} is the zero-phonon transition energy, with the absolute rate given by Eq. (7) multiplied by a factor on the order of the phonon frequencies active in the decay.

As an illustration of the theory, Huang and Gu have used a five-frequency-group model in which that lattice relaxation energy is held constant for each group, i.e., for $\hbar\omega_t = t\hbar\omega_0$, $S_t = S_0/t$ for $t = 1,2,\ldots,5$. Comparison to calculations made using the general theory of multiphonon decay give consistent results. The SCC model corresponding to these values of S and $\hbar\omega_0$ yields results for the nonradiative decay which are too small by many orders of magnitude.

Huang and Gu then applied the above model to the specific case of the ${}^4T_1$-${}^6A_1$ transition in CMC-H and CMC-D, noting that the high-frequency vibrations of the O-H or O-D stretch modes must be reflected in their grouping of the phonons. The parameters found to give results consistent with the observed sidebands and lifetimes were as follows for CMC-H:

$$\hbar\omega_0 = 90\ \text{cm}^{-1},\ \hbar\omega_t = t\hbar\omega_0 \ \text{for } t = 1\text{–}4\ ,$$

$$\hbar\omega_5 = 25\hbar\omega_0 = 2250\ \text{cm}^{-1}\ ,$$

$$S_t = S_0/t \ \text{ for } t = 1\text{–}4\ ,\ S_5 = S_0/50\ ,$$

$$S_0 = 5\ ,\ S = 10.5\ ,$$

and the same for CMC-D except for the following changes in the high-frequency group, to reflect the changes due to deuteration:

$$\hbar\omega_5 = 18\hbar\omega_0 = 1620\ \text{cm}^{-1}\ ,\ S_5 = S_0/36\ .$$

The groupings above are qualitatively consistent with the bulk-phonon modes principally engaged in the formation of the sideband and with the modes associated with the H_2O or D_2O molecular vibrations. The Huang-Rhys factors for the latter groups were reduced by an arbitrary factor of $\frac{1}{2}$ to account for the weaker coupling of these modes to the active center.

The predicted multiphonon decay rate at the zero-phonon transition energy is 50 and 5×10^{-3} s^{-1} for CMC-H and CMC-D, within an order to magnitude agreement with the CMC-H fluorescence lifetime. As calculated, the high-frequency modes in the models have energies of 2250 and 1600 cm^{-1} for CMC-H and CMC-D, respectively, and therefore do not accurately reflect the infrared spectra observed. The S factors resulting from these models are also too large compared to the experimentally determined values.

We have recalculated the phonon sideband profiles and the corresponding multiphonon transition rates using a computer program based on the Huang-Gu theory. We have incorporated in this program the observed O-H and O-D vibrational frequencies and the experimentally observed S factor.

The values obtained in our fits to the observed sidebands are as follows:

$$\hbar\omega_0 = 90\ \text{cm}^{-1},\ \hbar\omega_t = t\hbar\omega_0 \ \text{for } t = 1\text{–}4\ ,$$

$$\hbar\omega_5 = 36\hbar\omega_0 = 3240\ \text{cm}^{-1}\ ,$$

$$S_t = S_0/t \ \text{ for } t = 1\text{–}4\ ,\ S_5 = S_0/216\ ,$$

$$S_0 = 4.55\ ,\ S = 9.5$$

for CMC-H, and the same for CMC-D with the following changes in the high-frequency group: $\hbar\omega_5 = 27\hbar\omega_0 = 2430\ \text{cm}^{-1}$ and $S_5 = S_0/162$. The fit obtained for CMC-D is shown in Fig. 3, along with the observed sideband. The calculated shape can be seen to give very good agreement with the observed sideband.

The calculated multiphonon relaxation rates are 32 and 5.9×10^{-2} s^{-1} for CMC-H and CMC-D, respectively, again in reasonable agreement with the observed lifetime of CMC-H. Note that the lattice relaxation energy of the high-frequency group in this model is one-sixth that of the low-frequency modes.

V. DISCUSSION AND CONCLUSION

We have shown that multiphonon effects are radically affected by deuteration of CMC. We have used a new model proposed by Huang and Gu to explain the observed properties which could not be adequately described by the SCC model. The Huang-Gu model, as it was noted, is a simple but useful extension of the SCC model which incorporates the effects of different groups of phonons

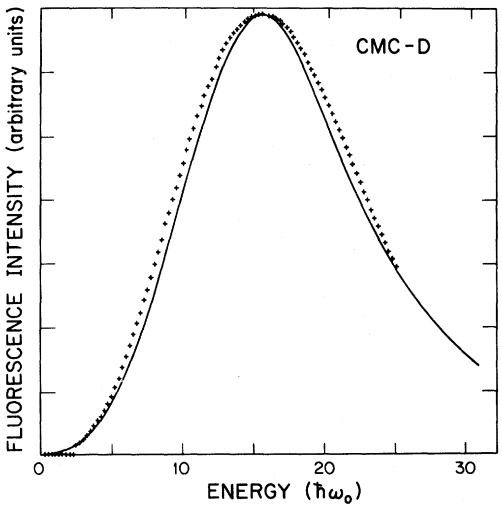

FIG. 3. Solid line is the phonon sideband predicted from the model developed in this paper for CMC-D. Crosses are observed sideband intensity in arbitrary units. Horizontal scale is in units of $\hbar\omega_0 = 90\ \text{cm}^{-1}$.

active in nonradiative processes. The model has allowed us to simultaneously consider the effects of both bulk and high-frequency vibrations on the sidebands and nonradiative transition rates of excitations in these materials.

Huang and Gu point out that the asymmetry observed in the sidebands is an indication of the presence of high-frequency phonons, with the degree of asymmetry correlated to the frequency and coupling of these phonons to the active center. These authors also note that greater accuracy can be obtained by increasing the number of phonon groups used in the model. For example, in the case of the hydrated samples, the effects of the vibrations at 1600 cm^{-1} could be included by adding a sixth group to the model. The point to be made, however, is that the model yields quantitative results in good agreement with the empirical results observed in deuteration of CMC and that these effects can be linked to a high-frequency group of phonons which are susceptible to isotopic shifts.

A subject which we have not addressed here is the shift observed in the position of the zero-phonon line in the deuterated sample. This shift of 18 cm^{-1} is likely due to the zero-point vibrations and should be the subject of further investigations.[14]

In conclusion we have presented an analysis of the multiphonon sideband and nonradiative relaxation processes in the $^4T_1$ state of CMC-H and CMC-D and shown that the results are consistent with the theory recently advanced by Huang and Gu. Both the asymmetry in the sideband and the short fluorescence lifetime observed in CMC-H are shown to be due to an isotope sensitive high-frequency vibration of the water molecules.

ACKNOWLEDGMENTS

We would like to thank Professor F. L. Roesler for the use of the infrared spectrophotometer used in obtaining the infrared data. We would also like to acknowledge with thanks the assistance and discussion provided by Dr. R. M. MacFarlane, Dr. E. Strauss, and Professor D. L. Huber. In addition, we thank Professor K. Huang for his continued interest and for providing us with his paper prior to publication. This work was supported by the National Science Foundation under Grant No. DMR-81-16733.

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