Table I. Values (in eV) of the exchange integral J for La:Ce and La:Gd alloys, of the position E of the $4f$ level, and its variation dE under a 10 kbar pressure in La:Ce alloys. Calculations are done with two densities of states, $n(E_F)=2.4$ and 0.5 states/eV atom, and with a half-width $\Delta=0.02$ eV. (Between brackets the pressures p are expressed in kbar.)

	$J_{Gd}=J_1$ (eV)	$J_{Ce}(p=0)$ (eV)	$J_{Ce}(p=10)$ (eV)	$E(p=0)$ (eV)	$E(p=10)$ (eV)	$dE=E(p=0)-E(p=10)$ (eV)
$n(E_F)=2.4$ states/eV atom	0.03	−0.08	−0.11	0.05	0.04	0.01
$n(E_F)=0.5$ states/eV atom	0.06	−0.18	−0.24	0.11	0.085	0.025

similar system, the Y:Ce alloys,[11] which are not superconductors, would also be very interesting to study at very high pressures. Both La:Ce and Y:Ce alloys show a Kondo effect and are good candidates to study experimentally the transition from magnetism to nonmagnetism at very high pressures when E becomes zero. This study would relate directly to all the recent theoretical developments on the Kondo effect.

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OBSERVATION OF A THERMODYNAMIC DISTINCTION BETWEEN BRILLOUIN ZONE CENTER AND BOUNDARY EXCITON STATES IN MnF_2

R. E. Dietz, A. E. Meixner, and H. J. Guggenheim
Bell Telephone Laboratories, Murray Hill, New Jersey

and

A. Misetich
Francis Bitter National Magnet Laboratory,* Massachusetts Institute of Technology, Cambridge, Massachusetts
(Received 19 August 1968)

The shape of the intrinsic-emission magnon sideband is well described assuming a wave-vector representation but with zero dispersion for the exciton. An observed difference in the decay rates of the intrinsic-emission zero-magon line and magnon sideband implies that the zone-center and zone-boundary excitons are distinct thermodynamic states. Thus, the exciton wave-vector states are, at least approximately, eigenstates.

A number of recent papers have been concerned with the properties of the optically excited states of MnF_2,[1] particularly those states belonging to the lowest $^4T_1$. These transitions have been classified as zero-magnon lines and magnon sidebands, both of which are zero-phonon lines, as well as broad phonon sidebands which are not relevant to this communication. In order to calculate the shapes of the magnon sidebands,[2-5] a Frenkel exciton representation has been assumed for these excited states wherein the zero-magnon lines correspond to the creation (in absorption) or the annihilation (in emission) of excitons near the center of the Brillouin zone ($\vec{k}=0$), while the sideband peaks correspond to the creation or annihilation of an exciton with the simul-

taneous creation (at low temperatures) or annihilation ("hot" bands) of a magnon, both particles having wave vectors near the zone boundary.

Recent experiments,[6] however, have demonstrated that the excitons must have an energy dispersion of less than 1 cm^{-1}, and that the magnon sideband shapes in absorption are largely determined by a strong magnon-exciton interaction. Since in emission the exciton and magnon do not exist simultaneously at low temperatures, the emission spectrum is free from this interaction complication, and as shown in Fig. 1, the shape of the magnon sideband of the intrinsic exciton in emission can be computed[7] from the neutron scattering density of magnon states[8] without any adjustable parameters, assuming zero dispersion for the exciton.

Thus, while we may say that an exciton (wave-vector) representation is sufficient to explain the observed sideband shapes, is it necessary? More explicitly, are the wave-vector states true eigenstates or merely a suitable basis? If the exciton consists of a stationary excitation localized on a particular atom, then its wave function may be expressed as a Fourier sum over all the wave-vector states of the Brillouin zone, there is no energy dispersion, and the exciton description is a trivial one, although useful in relating to the wave-vector basis of the magnon. (Such a localized description might be valid, for example, if the exciton were a small polaron of very large mass.) Therefore, a wave-vector representation for the excited state will be necessary only if the different wave-vector states are thermodynamically distinct, i.e., do not have fixed relative occupation numbers.

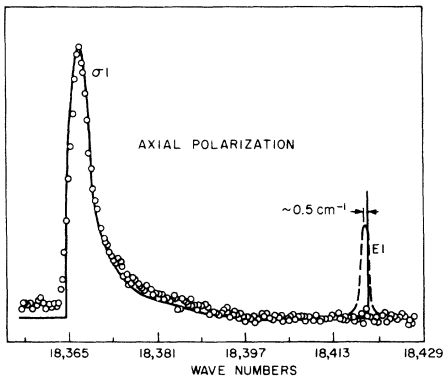

FIG. 1. Zero-phonon emission resulting from the decay of intrinsic excitons in MnF_2 at 1.3°K. The sharp line indicated by the dashed curve is $E1$, the magnetic dipole zero-magnon line, which is observed only in σ polarization. The broader peak $\sigma 1$ is the electric dipole magnon sideband which is observed in both σ, and as shown in the figure, axial polarization. The solid curve is a theoretical calculation of the sideband shape as outlined in Ref. 7. The error in predicting the frequency of the zero-magnon line (about 0.5 cm^{-1}) is less than the reported error of the neutron-scattering measurements.

In order to answer this question, we have measured the rate of decay of the zero-magnon and magnon-sideband emission, following pulse excitation of the excitons by the 5145-Å line of an argon-ion laser. The emitted photons were dispersed with a monochromator and detected with a photomultiplier, then discriminated and counted by conventional photon-counting techniques. Counts from repetitive pulses were stored in a multichannel analyzer for signal averaging. The results of these measurements are shown in Fig. 2(a) for 1.3°K and in Fig. 2(b) for 4.2°K.

As had previously[9-10] been pointed out, the bulk of the visible emission from MnF_2 arises from Mn levels perturbed by impurity ions such as Zn and Mg. These trapping levels occur some tens of cm^{-1} below the lowest intrinsic exciton. Other traps such as nickel emit in other regions of the spectrum,[11] and possibly still other traps decay nonradiatively. All told, trapping processes reduce the quantum efficiency for the excitation and lifetime of the intrinsic excitons by more than two orders of magnitude in the purest available crystals.[12] Thus the decay of the intrinsic excitons is dominated by nonradiative trapping processes rather than the radiative lifetime of about 35 msec.[13] As seen for 1.3°K in Fig. 2(a), the decay of the zero-magnon line and magnon sideband are similar and both are nonexponential. Nonexponential decay would be expected if the mobility of the excitons were small and the trapping cross sections large. However, at 4.2°K the rate of decay of the magnon sideband intensity is significantly increased from that of the zero-magnon line, while the zero-magnon decay is relatively similar to that at 1.3°K. Below about 2°K, the intensity of both lines is temperature independent, suggesting that the exciton transport and trapping is not thermally activated at low temperatures.

It is possible to draw several conclusions from these data without making further assumptions:

(1) The different decay rates at 4.2°K prove that the zone-center and near-boundary states are thermodynamically distinct. The similarity of rates at 1.3°K does not necessarily indicate the converse.

(2) At 4.2°K the zone-boundary and zone-center

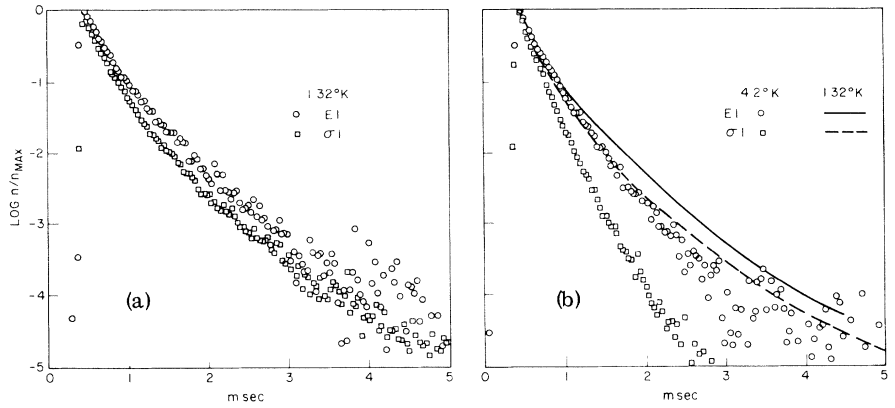

FIG. 2. Decay of the intensity of the zero-magnon line ($E1$) and the peak of the magnon sideband ($\sigma 1$) following pulse excitation at two temperatures. The spectral slit width in both cases was 1.5 cm^{-1} centered on the intensity peaks. The channel width was 25 μsec with 12.5-μsec dead time between channels. The laser pulse (rectangular wave) width was 25 μsec and the pulse interval was 7.5 msec. The pulse occured near the eleventh channel, with peak fluorescence attained by channel 13 or 14. The count in channel 14 was chosen for normalization. The ordinate is linear in the log of the relative intensity. The indicated intervals are powers of e. The curves in (b) summarize the data of (a). A background count was subtracted from each channel count. For $E1$ the background count was about 2% of the peak count, while for $\sigma 1$ it was less than 0.5%. The background was determined by averaging the count in the ten channels preceding the laser pulse. This count proved to be equal to the dark count determined independently.

excitons fail to attain quasiequilibrium (which would be evidenced by equal decay rates) during the span of time covered by Fig. 2(b), or about 3 msec. Thus, the wave-vector distinction between zone-center and zone-boundary excitons is limited by the trapping lifetime rather than by thermal scattering which would bring the system into equilibrium after a long time. Nearly elastic scattering of zone-center excitons into zone-boundary states by crystal imperfections must also be negligible.

(3) The exciton trapping probability at low temperatures (<2°K) is not thermally activated (i.e., involves only spontaneous phonon emission) and is independent of wave vector.

(4) The trapping probability of the near zone-boundary excitons is greater than for the zone-center excitons at 4.2°K.

Conclusions (1) and (2) suggest that a wave-vector representation is necessary to account for both the spectral measurements and the decay measurements at 4.2°K. However, to prove that a wave-vector representation is uniquely valid, we would have to demonstrate the thermodynamic distinctness of each wave-vector state. Not only is this impracticable, but the validity of the wave-vector representation will be limited by the dimension of the unperturbed regions of the crystal. In view of the narrowness of the exciton band, these regions may be small.

The significance of conclusions (3) and (4) is more difficult to speculate on since the trapping probability involves directly both the exciton group velocity and the trapping cross section.

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[7]Although we will present details of the calculation of the shapes of the emission magnon sideband of the intrinsic exciton in a future paper, we sketch the calculation briefly: Polarization studies of the emission for the crystal under (110) stress indicate that the relevant transition moment operator for the emission is

$P=\sum(P_{i,i-1}A_i a_{i-1}^{\dagger}+P_{i,i+1}A_i a_{i+1}^{\dagger})$, where A_i is an annihilation operator for ${}^4T_1$ excitation on ion i of sublattice A, and $a_{i\pm1}^{\dagger}$ creates a spin deviation on its first neighbor. The P's are interaction constants similar to those defined in Ref. 2. The exciton operators can be expressed as Fourier sums of the corresponding momentum operators A_k, as well as for the usual magnon operators $\alpha_k^{\dagger},\beta_k$. P is then given by $\sum_k P_k$, where the important terms P_k are $P_k=P_{001}\exp(ik_zc)u_kA_k\alpha_k^{\dagger}+P_{00\bar{1}}\exp(-ik_zc)u_kA_k\alpha_k^{\dagger}$, where u_k is the usual magnon sublattice weighting function. By considering the crystal symmetry, we obtain the components $\xi(110)$ and $\eta(1\bar{1}0)$ of the electric vector polarization which are $P_k^{\xi,\eta}=2iu_kP_{001}^{\xi,\eta}\sin(k_zc)$, where the ξ and η components are distinct for a sublattice exciton.

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[12]We have found that the trapping probability increases with temperature, and can be reduced by stressing the crystals uniaxially along the 001 direction. Such a stress is also sufficient to render the trapping probability nearly independent of temperature between 1.3 and 4.2°K. Since the intrinsic exciton emission is nearly invisible at 4.2°K in an unstressed crystal, all data recorded in Figs. 2(a) and 2(b) were made under a stress of 25 kg/mm^2.

[13]This is the low-temperature lifetime of the weakly perturbed traps, measured in Ref. 9, which have essentially the same wave function as do the intrinsic exciton states.

ZEEMAN EFFECT AND SYMMETRY OF THE INTRINSIC SnO_2 EXCITON

Masahiro Nagasawa
Wireless Research Laboratory, Matsushita Electric Industrial Co., Ltd., Kadoma, Osaka, Japan

and

Shigeo Shionoya
The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan
(Received 15 July 1968)

The Zeeman effect of the intrinsic SnO_2 exciton (direct forbidden) has been measured at 1.8°K, thus facilitating the identification as well as the interpretation of the anisotropic exciton spectra. The exciton symmetries and possible band symmetries are obtained on the basis of group theory and appear to be consistent with the valence band of O $2p$ functions and the conduction band of Sn $5s$ functions, both being crystal field split.

In our previous report[1] the anisotropic absorption spectrum of SnO_2 (D_{4h} symmetry) at very low temperatures was described. Exciton structure composed of a series of sharp lines having absorption coefficients less than 100 cm^{-1} was found near the fundamental absorption edge (3.597 eV at 1.3°K) for light polarized perpendicular to the c axis. The crystals were transparent in this spectral region for light polarized parallel to the c axis. The photon energies of the exciton lines satisfy the relation for the hydrogenlike series beginning with the $n=2$ quantum state.

The situation where the $n=1$ state is totally inactive to light is expected to arise if the transitions between the Bloch states at either side of the direct gap are forbidden by selection rules, as in the case of Cu_2O.[2] However, it is not self-evident that this situation is the case in SnO_2, since the conduction and valence bands of this material may be considered to be s-like and p-like, respectively.

In the present Letter, measurements of the Zeeman effect are briefly described. The results facilitate the identification as well as the interpretation of the anisotropic exciton spectra. The exciton symmetries and possible band symmetries are obtained on the basis of group theory. It is shown that the experimental facts are not inconsistent with the valence band of O $2p$ functions and the conduction band of Sn $5s$ functions.

The measurements were made spectrophotometrically using a Spex Model 1700-II grating spectrometer in the second order (reciprocal dispersion, 5.5 Å/mm) and an EMI 6256S photomultiplier. The crystals, prepared by the vapor reaction method,[3] were cut into platelets of 0.2- to 0.5-mm thickness with the c axis in the plane. The crystals were immersed in liquid helium at