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Zero-Phonon Lines and Phonon Coupling in ZnS:Mn

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The optical absorption and emission spectra of several ZnS:Mn crystals (0.07 to 1.0 mole%) were obtained at 4.2 and 77°K. Fine structure was observed in all bands. The predominant structure was identified in terms of phonon emission coupled to one electronic transition in each band. Zero-phonon lines were found at 17 891, 19 683, 21 237, 22 638, and 25 297 cm^{-1}. They should correspond to transitions between some levels of the cubic crystalline field—terms such as $^6A_1\rightarrow{}^4T_1$, $^6A_1\rightarrow{}^4T_2$, $^6A_1\rightarrow{}^4E$, $^6A_1\rightarrow{}^4A_1$, etc. Principal phonons participating are of energies of about 86, (183,263), 298, and 340 cm^{-1}. Possible mode assignments are pointed out. In conclusion, we suggest that the usually observed widths and shape of manganese bands are due predominantly to phonon coupling.

INTRODUCTION

MANGANESE, it has been known for a long time, is an efficient luminescence activator in a number of host lattices, e.g., silicates, sulfides, and fluorides of zinc or cadmium.[1] Characteristics of manganese activation are: First, the emitted light is concentrated in a spectral band of 500 cm^{-1}, with a maximum in ZnS at about 17 000 cm^{-1} (5860 Å). This half-width is much narrower than that of emissions activated by Cu or Ag, but, on the other hand, much wider than that observed in the luminescence of rare-earth activated crystals. Second, absorption measurements on crystals containing manganese usually show several absorption bands at energies above the Mn emission band. The absorption bands are simultaneously excitation bands, and absorption does not contribute to any photoconductivity to speak of within the host crystal. For ZnS:Mn, Kröger[2] showed the existence of four absorption maxima at about 25 600 (3900 Å), 23 300 (4300 Å), 21 500 (4650 Å), and 20 100 cm^{-1} (4980 Å). A fifth absorption peak with smaller absorption coefficient has also been observed. It centers at 18 700 cm^{-1} (5350 Å).

From this evidence it was early postulated that the manganese luminescence and absorption of, e.g., ZnS:Mn must be due to an electronic transition within the manganese, which as a divalent ion could readily occupy the site of Zn^{2+} in the ZnS lattice. The ground state of the free Mn^{2+} ion, a d^5 configuration, will be a ^6S state, that is, a symmetrical arrangement with all five spins parallel. The first excited state will be a ^4G state with one spin antiparallel, and so on. Transitions from the ground state to those excited states, which are formed by spin reversal, are forbidden. The crystalline field perturbs the pure states and loosens the selection rules. The behavior of the Mn^{2+} states in a cubic crystalline field can be estimated from the calculations of Sugano and Tanabe.[3] For hexagonal ZnS the deviation from cubic symmetry is very small and can be neglected in first order. Qualitatively the correspondence between energy levels and absorption bands is obvious. One readily assigns the emissions to the lowest transition $^4T_1\rightarrow{}^6A_1$ and the absorption bands, counting from lower energies, to transitions from the $^6A_1$ ground state to the sequence of excited states $^4T_1$, $^4T_2$, ^4E, $^4A_1$, and so on, for some Dq value representative of the strength of the crystalline field of the host lattice.

Recently Curie,[4] among others, suggested that the Mn luminescence center is more complex and consists of something like a substitutional Mn^{2+} ion plus at least one Cl$^-$ ion or a vacancy as nearest neighbor. For such a center a strong uniaxial field on the Mn^{2+} would be a dominant perturbation and render useless any calculation according to the symmetry of the host lattice. The temperature behavior of absorption lines, however, will be shown to be consistent with the behavior expected from energy terms due to a crystalline field of cubic symmetry.

All the absorption coefficients of the different bands are relatively small, since the parent free-ion transitions are forbidden, and become allowed only through perturbations due to one or a combination of the following possible sources: crystalline field, spin-orbit interaction, exchange coupling of Mn^{2+} pairs, or phonon coupling.

The shape of the Mn emission band is also known to be non-Gaussian. Klick and Schulman,[5] more than ten years ago, in the case of the zinc silicate host lattice, have given an explanation for such behavior in terms of configuration coordinates and vibrational states. All

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* Presently on leave at Ecole Normale Superieure, Paris, France.

[1] See, e.g., C. C. Klick, J. H. Schulman, *Solid State Physics* (Academic Press Inc., New York, 1955), Vol. 5 or D. Curie, *Luminescence Cristalline* (Dunod Cie., Paris, 1960).

[2] F. A. Kröger, Physica Haag **6**, 764 (1939).

[3] S. Sugano, Y. Tanabe, J. Phys. Soc. Japan **9**, 753 and 766 (1954), reviewed by D. C. McClure, in *Solid State Physics* (Academic Press Inc., New York, 1959), Vol. 9.

[4] D. Curie, Compt. Rend. **258**, 3269 (1964).

[5] C. C. Klick and J. H. Schulman, J. Opt. Soc. Am. **42**, 910 (1952).

search for sub-bands, however, was without success at that time.

Recently McClure[6] reported on fine structure in two absorption bands of ZnS containing 0.5 to 11% Mn, which he interpreted on the basis of crystalline-field theory and spin-spin interactions of Mn ion pairs.

It is the purpose of this paper to report that all absorption and emission bands of ZnS:Mn at 4.2°K consist of a large number of sub-bands or lines as long as the Mn concentration is kept sufficiently low. Most of these lines we identify in terms of phonon emission coupled to a parent, electronic transition.

EXPERIMENTAL RESULTS

The ZnS single crystals used were of either predominantly hexagonal or nearly perfect cubic structure. The doping level was between 0.07 and 1.0 mole % Mn. Hexagonal samples were supplied by Don Naas of the Aerospace Research Laboratories, who grew them from the vapor phase. Also, melt-grown samples of hexagonal structure were obtained from the Eagle-Picher Company. The cubic sample was grown from the melt by Professor Shionoya at the Solid State Institute, Tokyo. The lines to be discussed were found consistently in all samples. There exists a scatter of a few wave numbers between samples when line positions are compared in the spectra. No systematic difference between samples of hexagonal and cubic structure was observable.

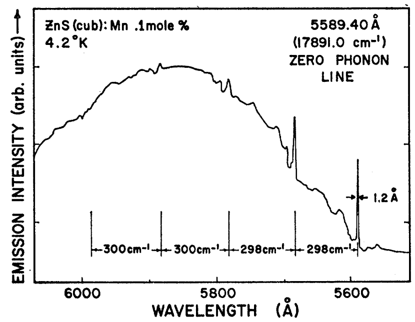

FIG. 1. Densitometer trace of the ZnS:Mn emission. The sample contains 0.1 mole % Mn.

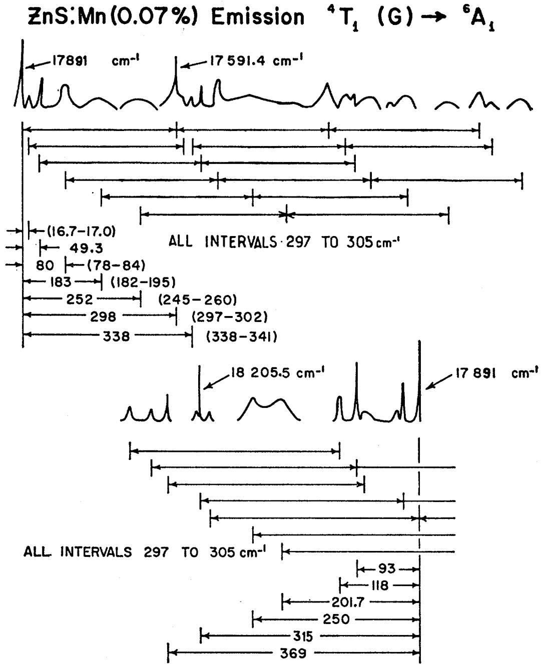

FIG. 2. Scheme of the structure observed on the emission band of several crystals containing 0.07% Mn. The most frequently recurring interval of 298–304 cm^{-1} is indicated by solid arrows. The upper part of the figure shows the structure extending toward the emission center. "Fundamental differences" are counted from the zero-phonon line (17 891 cm^{-1}). The lower part shows occasionally observed lines on the high-energy side of the zero-phonon line. Energy differences are indicated again in cm^{-1} with respect to the zero-phonon line. Solid arrows extending to the right of the 17 891 line indicate that repetitions of the corresponding high-energy line have been identified on the low-energy side of the zero-phonon line also.

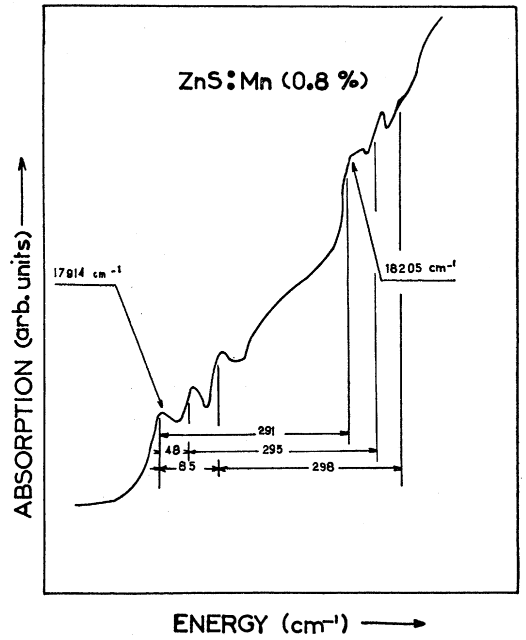

FIG. 3. Densitometer trace of the onset of the 18 700 cm^{-1} (5350 Å) absorption band. The sample contains 0.8 mole % Mn.

A densitometer trace of the luminescence band is shown in Fig. 1. One can very clearly recognize a structure at the high-energy side of the maximum. This structure appears to be repeated periodically and becomes less distinct toward the peak of the emission band. The period corresponds to an energy of roughly 300 cm^{-1}. Figure 2 shows a schematic summary of all emission lines which were observed in different crystals. Again, the repetition in a 300-cm^{-1} period is most obvious. In the upper part of the figure, there are other, "fundamental" energy differences indicated: 16.7, 49, 80, 183, 252, 298, and 340 cm^{-1} (maximal and minimal values in brackets). These differences are counted from

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[6] D. C. McClure, J. Chem. Phys. 39, 2850 (1963).

the 17 891 line toward lower energies. On the high-energy side of the 17 891 line, we also see some structure, but of much lower intensity and in part not consistent for different crystals. This structure is shown in the lower part of Fig. 2, counting the energy differences from the 17 891 line toward higher energies. Occasionally one also finds repetitions of these "high-energy" lines at a 300-cm^{-1} period which is indicated by the solid arrows. It is to be noted that all lines of which a repetition at 300 cm^{-1} is observed are considered as "fundamental differences" from the 17 891 line. We find, e.g., one such repetition for the line which is 17 cm^{-1} off and also two such repetitions for the line placed 340 cm^{-1} toward the emission maximum.

The spectrum of the electroluminescent emission was identical to that of the photoexcited emission with excitation through any of the five absorption bands.

With increasing Mn content, lines broaden and shift slightly toward higher energies. The structure toward the center of the emission band also becomes less distinct. Samples with 1.0% Mn content show recognizable structure only between 17 880 and about 17 580 cm^{-1}.

Similarly we observe structure in absorption, which appears on the low-energy side of the absorption band maxima. Again, the most accurate determinations are made and the sharpest structure is obtained with crystals of 0.07 to 0.1% Mn content. Because of the low absorption coefficient, however, and the limited dimensions of our crystals (we used up to 2.5-cm effective absorption length by internal reflections), studies on some of the absorption bands could be made only with Mn concentrations of 0.8%. Qualitative features and less accurate line separations can be deduced also from those spectra, as becomes apparent by a comparison of a spectrum of 0.8% Mn concentration to one of 0.07%, for two absorption bands (20 100 and 21 500 cm^{-1}) where the absorption coefficients are high enough to allow the absorption to be recorded with available crystals of the lower concentration.

The first absorption band, with a maximum at 18 700 cm^{-1}, is the weakest, and thus measurements could be made only on samples with high Mn concentrations. The structure which is observable on the low-energy side of the absorption maximum is shown in Fig. 3. At the onset of absorption one finds three lines with the same characteristic energy intervals as in emission, namely 48 and 85 cm^{-1}, and a less distinct repetition of the triplet displaced roughly 295 cm^{-1} toward higher energies, i.e., toward the maximum of the absorption band. The lines are broad, and a repetition can be recognized only once because of the high doping level, similar to what had been observed in the emission for crystals with high Mn content. The lowest energy line in the absorption structure is at 17 914±5 cm^{-1}. We believe that it is electronically of identical origin to that of the 17 891±0.5-cm^{-1} transition observed in emission, which, for equal Mn content appears at 17 905±5 cm^{-1}. The spectra taken with higher Mn concentrations furnish considerably less reliable values. Thus we think we see in absorption a mirror image of the structure we saw in emission.

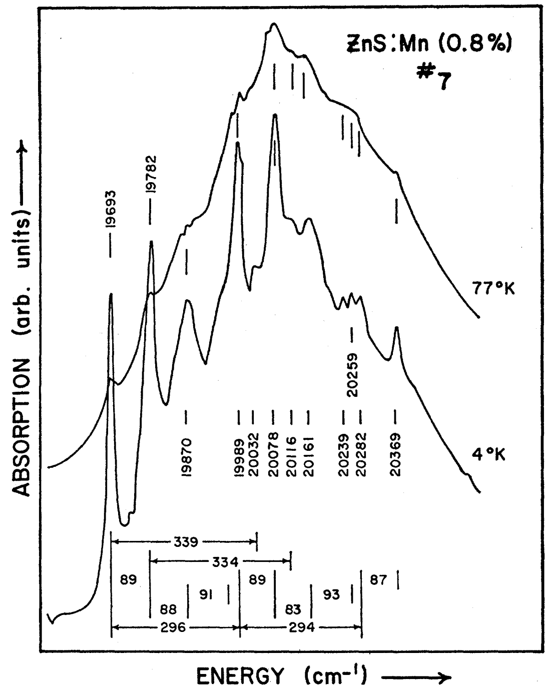

FIG. 4. Densitometer trace of the 20 100 cm^{-1} (4980 Å) absorption band at 4.2 and 77°K for a crystal containing 0.8% Mn.

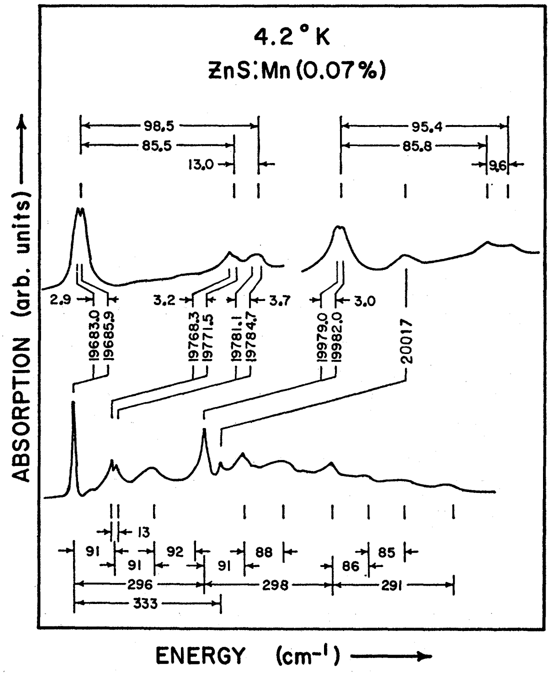

FIG. 5. Densitometer trace of the same absorption band shown in Fig. 4 of a crystal containing 0.07 mole % Mn. The upper curves show the fine splitting on an expanded scale.

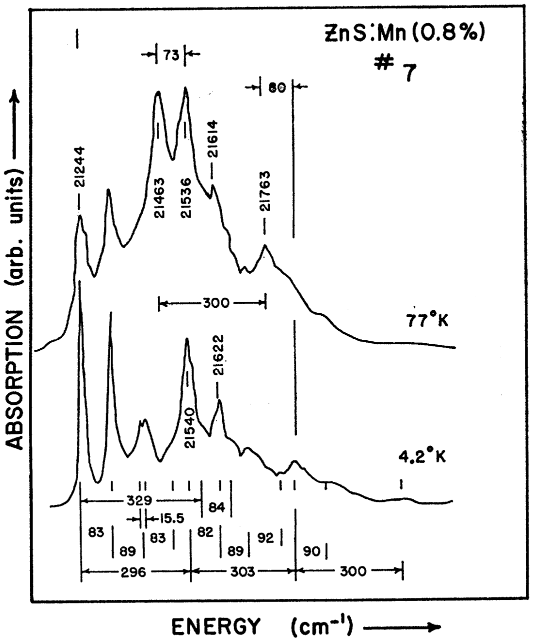

FIG. 6. Densitometer trace of the 21 500 cm^{-1} (4650 Å) absorption band at 4.2 and 77°K of a crystal containing 0.8% Mn.

The second absorption band exhibits the structure shown in Fig. 4. At 77°K this structure is not very distinct. A comparison can be made with Fig. 5 which shows similarly a densitometer trace of the same absorption band for a 0.07 mole % concentration of Mn in ZnS. On the extended scale in the upper part of Fig. 5, one observes fine splitting of some of these lines.

Figures 6 and 7 show the corresponding traces of the 21 500 cm^{-1} band. We see again lines of remarkable sharpness and with sequences similar to those seen in the previous figures. In contrast to the transitions in Fig. 4, the structure in Fig. 6 still remains distinct at 77°K. Three of the intervals in Fig. 2, namely, those of 80, 183, and 252 cm^{-1}, are probably similar in origin to those of 91, 182, and 274 in Fig. 5 and to those of 87, 178, and 263 cm^{-1} in Fig. 7. The equidistant spacings of the corresponding lines in absorption might indicate that these differences should not be considered to be "fundamental" but rather are the repetition of an interval of 88 to 91 cm^{-1}, as indicated in Figs. 4–7.

The 23 300- and 25 600-cm^{-1} bands show structure too, though less clearly. For completeness we add the traces of the absorption spectra of a 0.8% sample in Figs. 8 and 9.

ZERO-PHONON LINES

The fact that emission has its mirror image in the lowest absorption band confirms our original assumption[7] that the origin of most lines composing the emission band and the absorption bands should be phonon emission coupled to an electronic zero-phonon transition. This is certainly true for the emission band and its mirror image, the lowest absorption band. By analogy we assume that a similar process determines the composition of the higher absorption bands, and we would like to suggest that the strong line of lowest energy in each band is a zero-phonon line, due to a transition of electronic origin. Thus we determine electronic transitions which have energy-level differences of 17 891, 19 683, 21 237, 22 638, and 25 297 cm^{-1}.

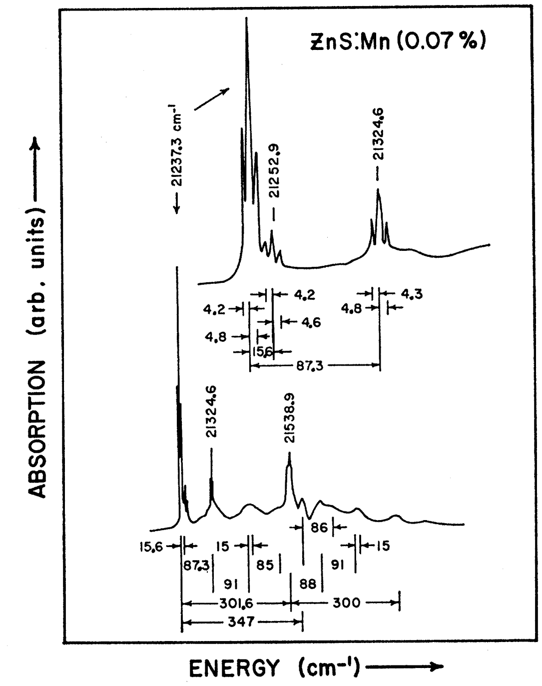

FIG. 7. Densitometer trace of the same absorption band shown in Fig. 6 of a crystal containing 0.07 mole % Mn. The upper curve shows the finer splitting on an expanded scale.

With respect to crystalline-field calculations for cubic symmetry the following term assignments seem reasonable, as they have been suggested before: 17 891 is the $^6A_1 \leftrightarrow {}^4T_1$, 19 683 the $^6A_1 \rightarrow {}^4T_2$, and 21 237 cm^{-1} is the $^6A_1 \rightarrow {}^4E$ and/or the $^6A_1 \rightarrow {}^4A_1$ transition. The temperature dependence of the zero-phonon lines and actually of all lines in the individual bands can be regarded as a good confirmation of this assignment: The lines of the emission band vanish at temperatures much lower than 77°K; those of the second band smear out considerably at 77°K (compare Fig. 4), while the lines of the 21 500 band remain distinct even at 77°K (Fig. 6). Such behavior is exactly that to be expected for one level strongly dependent on the crystalline field, one less dependent and one independent, which is just the nature of the assigned levels. We do not agree with McClure's[6] assignment of his 21 270-cm^{-1} line to the transition to the ^4E state and of the 21 555-cm^{-1} line to

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[7] S. Ibuki and D. Langer, J. Phys. Soc. Japan **19**, 422 (1964).

transitions to the ${}^4A_1$ state. These two peaks correspond to what we saw as lines at 21 237 and 21 539 cm^{-1}, with lower Mn concentrations. The energy difference of 302 cm^{-1} has recurred too frequently in all structured bands for us to feel justified in attributing it to the separation of two different electronic states.

The assignments of the higher absorption peaks are still somewhat doubtful. Again the temperature dependence of the line widths indicates a strong crystalline-field dependence of these levels. A crystalline-field calculation carried out by R. Euwema[8] using $F_2 = 56\,185$ and $F_4 = 33\,409$ cm^{-1}, which was derived from a best least-squares fit to our (${}^4T_1$), (${}^4T_2$), and (${}^4E,{}^4A_1$) zero-phonon lines, suggests that the 22 638-cm^{-1} line may belong to the ${}^2T_2(I)$ and the 25 297-cm^{-1} line to the ${}^4T_2(D)$ transition. The best Dq value for this fit of the lowest three levels was 480 cm^{-1}. The least-squares fit to the lowest three levels is not very good and leaves differences of up to 500 cm^{-1}. Similar differences, however, exist also if one does a least-squares fit to the free-ion values of Mn^{2+}. The transitions from the ground state ${}^6S$ to the ${}^2I$ level, connected with a spin change of two, are more strongly forbidden in the free-ion state than those to the quartet levels. In the crystalline field, however, and in the presence of phonons acting as perturbation, the ${}^6A_1 \rightarrow {}^2T_2$ transition might not be as improbable in comparison to transitions to quartet levels as in the free-ion case. Admittedly, this is somewhat speculative. The main justification for assigning the 22 638-cm^{-1} line to a transition to the ${}^2T_2$ level is that there is no other level between the fairly well-fitted ${}^4E$, ${}^4A_1(G)$, and ${}^4T_2(D)$ levels.

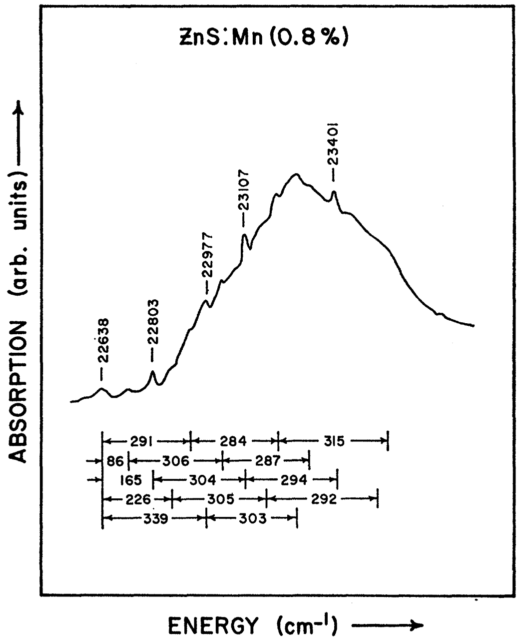

FIG. 8. Densitometer trace of the 23 300-cm^{-1} (4300-Å) absorption band. The Mn concentration is 0.8%.

PHONON LINES

Besides the existence of the mirror image, the following supports the assumption of phonon coupling: There are certain energy differences which recur similarly in all bands and which should be connected with vibrational structure, since recurrence of the structure due to a split ground state can be ruled out. There is no spin-orbit splitting of the ground state, and its crystalline-field splitting[9] is 2.77 10^{-3} cm^{-1}. The spin-orbit splittings of the excited states should differ considerably for the various states. Also, only vibrational structure would be expected to recur in periods.

Table I shows values of vibrational frequencies of the ZnS lattice and mode assignments when they have been made. The transverse optic (TO) determinations in parenthesis were made by the *Reststrahlen* method. All other values were derived from multiple phonon absorptions in the infrared spectrum. The agreement of the authors is not complete. The italicized values in the table are the ones which are close to the frequently recurring values of line separations in the ZnS:Mn spectra.

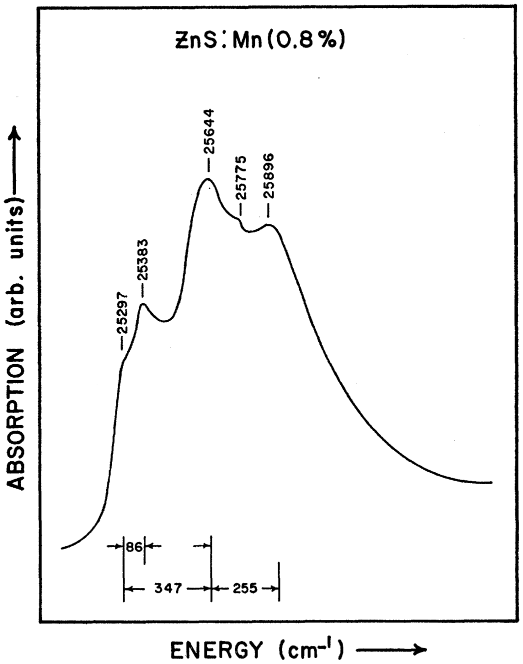

FIG. 9. Densitometer trace of the 25 600-cm^{-1} (3900-Å) absorption band. The Mn concentration is 0.8%.

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[8] R. Euwema (to be published). [F values are used according to C. Nielson and G. Koster, *Spectroscopic Coefficients for the p^n, d^n, and f^n Configurations* (MIT Press, Cambridge, Massachusetts, 1963).]

[9] H. Azarbayejani, Final Report of University of Michigan under Contract AF 49(638)987, January, 1963, Part III, p. 7 (unpublished).

TABLE I. Phonon energies in ZnS. The reported phonon energies of the pure ZnS lattice are listed. The values in parenthesis were derived from *Reststrahlen* data; all others, from analysis of multiphonon absorptions. Assignments, when made by the authors, are indicated. The italicized values are to be compared with the energy differences which we found to occur frequently in the ZnS:Mn spectra.

Energy (cm^{-1})							Temp. (°K)	Structure	Reference
379			*297*	263	228		77	cubic	[a]
379			*298*	262	227		15	cubic	[b]
								hexagonal	
	350 LO$_\Gamma$	(310) TO$_\Gamma$		(274) TO$_\Gamma$			300	hexagonal	[b]
377 LO	*339* LO$_\Gamma$	(312) TO$_\Gamma$	*298* TO		*190* LA	115 TA	300	cubic	[c]
	346 LO	318 TO	*297* TO		*181* LA	*92* TA *73* TA	300	hexagonal	[c]
378 LO$_\Gamma$		(312) TO$_\Gamma$					300		[d]
366 LO$_\Gamma$	*349* TO$_\Gamma$	321 TO$_L$	*305* TO$_X$	272 LO$_L$ 275 LO$_X$	227 LA$_L$ 221 LA$_X$		77	cubic	[d]

[a] T. Deutsch, in *Proceedings of the International Conference on Semiconductors, Exeter 1962,* (The Institute of Physics and Physical Society of London, London, 1962), p. 505.

[b] M. Balkanski, M. Nusimovici, and R. Le Toullec, J. Phys. Radium **25**, 305 (1964).

[c] R. Marshall and S. S. Mitra, Phys. Rev. **134**, A1019 (1964).

[d] F. A. Johnson (to be published).

Of the crystals of 0.07 to 0.1% Mn concentration, the most obvious energy differences and periods which occur in several bands are summarized in Table II. The most frequent and most distinct repetition occurs at intervals of about 298 cm^{-1}, the energy that can also be found in nearly all determinations of lattice phonons. As this energy was assigned to a TO mode by Marshall and Mitra, and it is not far from Johnson's corresponding TO mode, we follow this assignment. The peak separated from the zero-phonon line by 80 to 90 cm^{-1} is as distinct, except in the ^4E, $^4A_1$ transition. The low frequency suggests the assignment of a transverse acoustic (TA) mode. The value is also in fair agreement with Mitra's TA values. The higher frequencies of about 193 and 263 cm^{-1} might actually be multiples of the TA mode or a longitudinal acoustic (LA) mode or LA+TA modes, respectively. The peak at 340 cm^{-1} usually occurs weakly but distinctly. Its energy separation seems to fit the frequency assigned to an LO vibration by Balkanski and Mitra and to a TO vibration by Johnson. In the lower part of Table II, we have followed the former assignment.

We have been tempted to evaluate the single-phonon lines and the phonon-coupled bands in terms of the optical analog of the Mössbauer effect,[10] whereby the integrated absorption (or emission) of the single-phonon line (I_s) compared to the absorption (or emission) of the associated band (I_b) can be connected to the zero-point bandwidth H and the most probable number S of phonons involved in the transition by the following expression[11]:

$$I_s/I_b=e^{-S}\approx\exp[-(H/2.5\hbar\omega_D)^2],$$

where ω_D stands for the frequency of the vibrational mode, which dominantly determines the broadening. Such an analysis, however, did not appear very meaningful to us at this point. Apart from the fact that one should consider at least two vibrational modes (TA and TO) and their mixtures, it seemed that the corresponding coupling constants are not independent of the Mn concentration. This can be seen by comparing the areas under the 21 237-, 21 325-, and 21 539-cm^{-1} peaks in Fig. 6 with the areas under the corresponding peaks (21 244, 21 337, 21 540) of the 4.2°K curve in Fig. 7.

TABLE II. Phonon energies in ZnS:Mn bands.

Transition	Line separation in cm^{-1}				
$^6A_1\leftarrow{}^4T_1$	78–84	182–195	245–260	297–302	338–341
$^6A_1\rightarrow{}^4T_2$	91	182	274	296–298	333
$^6A_1\rightarrow{}^4E,{}^4A_1$	87	178	263	300–302	347
Modes:	TA	2TA,LA	3TA,LA+TA	TO	LO

There are slight differences between our values for phonons in ZnS:Mn and some values reported for the phonons in the pure ZnS lattice. There are also slight but consistent differences of the same phonon energies observed in different bands. This might be explained by the fact that actually the lattice is perturbed locally by the Mn impurity and that different excited states form different perturbation centers in the ZnS lattice. It is to be noted that experimental accuracy, where line-width permitted, has been high enough to determine these differences within one wave number.

UNIDENTIFIED LINES

More lines were observed than those dealt with in the previous sections. We may mention, for example, those with energy separations of 4 and 16 cm^{-1} from the 21 237-cm^{-1} line, those with differences of 3 and 13 cm^{-1} in the second absorption band, and those 17 and 49 cm^{-1} toward lower energy, and all lines toward higher energy from the 17 891-cm^{-1} emission line. We have tried, so far unsuccessfully, to associate some of these lines with spin-orbit terms of the crystalline-field states using results of Euwema's calculations.[8] Minor

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[10] E. D. Trifonov, Dokl. Acad. Nauk SSSR **147**, 826 (1962) [English transl.: Soviet Physics—Dokl. **7**, 1105 (1963)].

[11] D. B. Fitchen, R. H. Silsbee, T. A. Fulton, E. L. Wolf, Phys. Rev. Letters **11**, 275 (1963).

lines as they are, they could also be associated with some centers of different symmetry. Lines with 15- and 49-cm^{-1} separations might also be due to phonon difference frequencies as Sugano[12] suggested. Also, there was no compelling reason to associate any of these lines we observed at 4°K with transitions between exchange-coupled ion-pair states.

CONCLUDING REMARKS

On the basis of the spectroscopic evidence we suggest that coupling by phonons is the predominant factor accounting for the usually observed band widths of Mn absorptions in ZnS and for the band width and non-Gaussian distribution of the Mn emission in ZnS. Since we recently observed similarly structured emission of Mn-activated CdS and structure in the absorption bands of ZnSe:Mn, it is probably safe to state that the process described is not restricted to the ZnS host lattice but might apply to divalent manganese as a luminescence and absorption center in general.

ACKNOWLEDGMENTS

We wish to thank Dr. R. Euwema for his help and interest in many discussions and for communicating to us the results of his calculations prior to publication. We are very obliged to the contributors of the crystals we used and to Dr. F. Chan for their x-ray analysis.

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[12] S. Sugano (private communication).

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Impurity Conduction in the Intermediate Concentration Region*

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The impurity conduction in semiconductors in the intermediate impurity concentration region is investigated theoretically by using the data available on antimony-doped germanium with small compensations. The origin of the activation energy ϵ_2 which characterizes the resistivity in a certain temperature range is discussed on the basis of the D^--band model, which is provided by the formation of a band as a result of the interaction between the states of negatively charged donors, the D^- states. The hydrogenic model is employed for the donor ground state, and we assume that the wave function describing the behavior of an electron in the weakly bound D^- state is of an exponential type. By using the tight-binding approximation, it is shown that the interaction between these states leads to the formation of the D^- band. Thus, the energy gap from the donor ground state, which is assumed to be localized, to the bottom of the D^- band is related to the observed activation energy ϵ_2. The numerical estimations are in qualitative agreement with the observed values.

I. INTRODUCTION

THE impurity conduction which is observed in semiconductors containing impurities at low temperatures has been recognized as having three different types of mechanism corresponding to the concentrations of impurities, i.e., low-, intermediate-, and high-concentration regions,[1,2] respectively.

At low concentrations, the effect of electron correlation dominates the electrical conduction.[2,3] The electrons (in what follows, the terminology is applicable to n-type samples) are localized at impurity sites and the electrical conduction takes place through the hopping processes of electrons from occupied to unoccupied sites with the aid of phonons, if there are any neighboring vacant sites as a result of compensation.[2,4]

At high concentrations, the interaction between impurities which are distributed at random is so strong that the so-called impurity band is formed.[5,6] The electrons behave like a degenerate Fermi gas in the band and the transport properties are metallic in nature.[3] The main cause of scattering is the random distribution of impurities itself and therefore the resistivity is independent of temperature.[7]

At intermediate concentrations, $0.6\sim 1\times 10^{17}$ cm^{-3} in the case of Sb-doped Ge, the electrical conductivity is

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[1] H. Fritzsche, J. Phys. Chem. Solids **6**, 69 (1958); H. Fritzsche and M. Cuevas, Phys. Rev. **119**, 1238 (1960).

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