Local vibrations at vacancies and the nature of the T_1-S_0 emission band of M centers in ZnS

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The main local vibration of F centers and M centers are calculated with the use of a simple spring-mass model. The model is applicable if the displacement of the surrounding ions from their lattice position is small. At the nodal points of the vibrations the surrounding region is replaced by a fixed wall. The respective spring constants are derived from the LO (L) phonon frequency $\Delta_3 = 338.6$ cm^{-1}. No adjustable parameters are used. The frequencies calculated are $\Delta_0 = 87.5$ cm^{-1}, $\Delta_1 = 124.0$ cm^{-1}, and $\Delta_2 = 261.5$ cm^{-1} in good agreement with the experimental values. Other local vibrations suffer strong damping and do not produce sharp phonon satellites. With the use of the energies of those local modes and of the LO (L) phonon the M-center emission is reevaluated. The emission results from two zero-phonon lines. Almost all the lower-energy spectral features are assigned as phonon satellites. The higher-energy satellites' intensity varies for different crystals and they are attributed to M centers near crystal defects.

I. INTRODUCTION

Imperfections in semiconductor crystals have electronic energy levels located between the valence and the conduction band. Recently centers with deep energy levels have been investigated with increasing interest. In crystals with predominant ionic binding such centers are formed by certain impurity ions or vacancies.

Special attention is paid to the vacancies of host lattice anions loaded with suitable numbers of electrons, as F and M centers. These centers have the advantage of almost perfect charge compensation and of a simple electronic structure similar to hydrogen. There electronic levels result from the local potential only and are not influenced by additional interactions as in the case of impurity centers.

Both local vibrations and bulk phonons influence the deep levels, and the details thereof can be understood only if their interaction parameters and frequencies are known. Current theories use arbitrary free adjustable parameters to obtain agreement with experiments.

This work will present a very simple acoustic model for local phonons at vacancies and will exemplify it for the case of the M center in ZnS. With this model it is possible to calculate the frequencies of local vibrations by using the masses of vibrating atoms and the derivative of the interaction potential of neighboring atoms known from the LO phonon

frequencies of the host lattice which are both known from experimental data. In the case of strong distortions the derivative is used as the only adjustable parameter, the same as for all local vibrations.

Evidence for an M center in an II-VI compound was first reported for ZnS.[1] From optical spectra the electronic structure of the M center was derived including the position of the ground state in the band gap and the energies of the first excited singlet and triplet states. An important experimental result was the identification of the emission of the lowest triplet state to the ground state, an emission band structured by more than 70 sharp lines (Fig. 1). The structure of this emission band could not be identified at that time. It was realized then that the structure of the emission band is composed of phononlike satellites. Six fundamental energy differences $\Delta_1-\Delta_6$ had been observed. One of them,

$$\Delta_3 = 338.6 \pm 0.3 \text{ cm}^{-1},$$

is obviously the LO (L) phonon of cubic ZnS. The nature of the five other energies and which of the more than 70 lines is the zero-phonon line was not known. All this will find simple explanations by the model presented.

II. THE M CENTER IN CUBIC ZnS

The M center in ZnS is formed by two neighboring F centers which are sulfur vacancies. Because
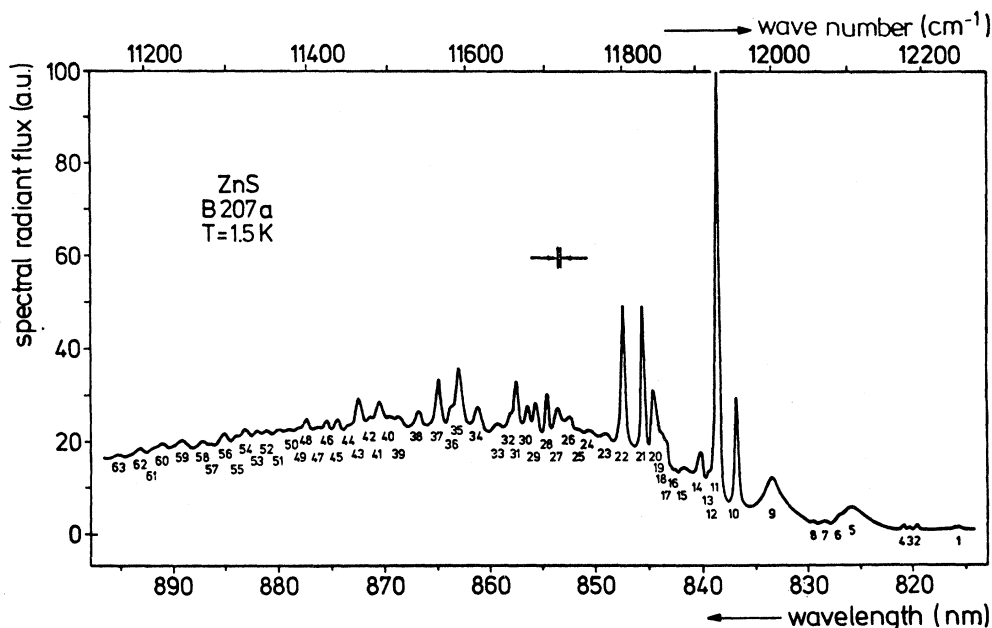
FIG. 1. Emission spectrum of the M center in ZnS at low temperature. Reproduced from Broser *et al.* (Ref. 1).

the effective charge of an F center is $q(F^{2+})=1,15e,$[2] each vacancy can bind one electron. Figure 2 shows the surrounding of the M center in ZnS. Each of the two S vacancies has four Zn ions as nearest neighbors. Six of those have three S neighbors instead of four as a Zn ion has normally in ZnS. The fourth binding is to the electron at the vacancy. One Zn ion (in the center) has two S neighbors only and both vacancies as neighbors. The magnitude of the local distortions at the M center is the essential factor for the applicability of the model. No adjustable parameter is required if this distortion is small, as argued below for ZnS.

The model presented and the spectral features discussed apply to an M center with both vacancies filled by an electron. The spatial extent of these electrons can be described by Bohr radii.[3] They are localized in the region between their respective four nearest Zn neighbors. The static displacement of these Zn ions from their perfect lattice positions results from the change in ionic and covalent binding forces[4] compared to the no-vacancy case. The respective Zn ions are bound to the vacancy and two or three sulfur ions. Static Coulomb interaction tends to force the Zn ions away from the vacancy because the effective charge of the vacancy is 15% higher than that of an electron.[2] However, the spatial extent of the electrons (Bohr radii of 1.3 Å in the ground state and 2.15 Å in the excited state) reduces this effect due to nonlinear interaction. Both the ionic and the covalent binding potential to

the sulfur neighbors are essentially the same. They further reduce any static displacement of the Zn ion away from the vacancy. Long-range forces on the Zn ion are hardly influenced by the vacancy and favor the position of the perfect lattice.

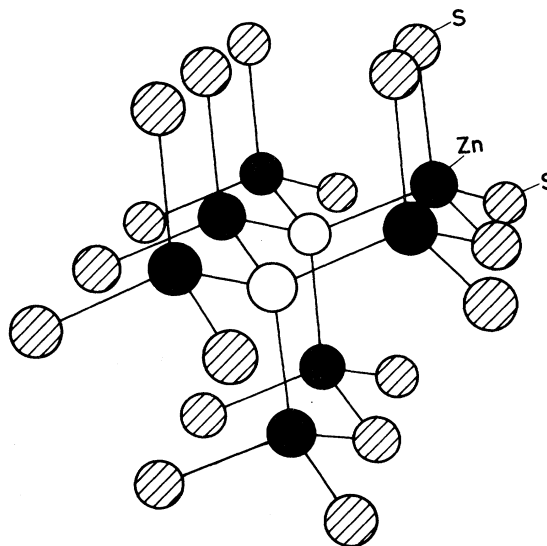The magnitude of the short-range forces can be

FIG. 2. The M center in ZnS and its surrounding. The black balls represent the zinc ions, the shaded ones sulfur ions.

obtained using the frequencies of the optical phonons and the magntiude of the long-range forces by combining the macroscopic elastic coefficients and the frequencies of optical phonons. Using well-known data the short- and long-range forces were estimated to be about the same magnitude. Taking into account all the effects mentioned, it was estirñated that the difference of the charges of the vacancy and the electron causes a change of less than 5% in the forces acting on the Zn ions nearest to the M centers. The resulting local distortion is small and can be neglected for the simple model of local vibrational modes.

III. LOCAL VIBRATIONS AT THE F CENTER AND THE M CENTER IN ZnS

The bulk lattice dynamic of ZnS is well understood[5,6] and the local vibrations of substitutional impurities have been reported for ZnS, InP, and GaP.[7] Local vibrations of F centers have been studied for alkali halides,[8,9] but not for II-VI compounds. Elastic displacement at the interaction of vacancies have been studied[10] and frequency spectra of disordered chains have been calculated.[11]

The local modes of vacancy are vibrations of the ions around it; obviously the vacancy cannot vibrate itself. These local vibrations are a complicated many-body problem despite the symmetry properties, mainly because of the frequency-dependent complex acoustic impedance of the surrounding region. Nevertheless, the main frequencies of the local modes of the M center can be calculated surprisingly accurately with the help of the simple and intuitive spring-mass model without resort to adjustable parameters or unjustified assumptions. The model can be simple because most of the fundamental modes of a vacancy center can be anticipated. Once a fundamental mode has been recognized the position of the nodes of the vibration can be determined. At these nodes the surrounding region can be replaced by a fixed wall.

A further simplification to one dimension is obtained from symmetry considerations for both the crystal and the ions' displacements in the particular mode. By then the problem has been reduced to the vibration of a linear chain with renormalized masses 'and·spring.,constants.

To begin with, the model is applied to a particular resonance of the perfect lattice to examplify the procedure and to derive a spring constant needed later. This resonance is the LO (L) phonon which is the highest-frequency longitudinal-optical phonon propagating in [111] direction. This is depicted in Fig. 3 for ZnS. The LO (L) phonon is a standing wave and neighboring ions vibrate against each other. The
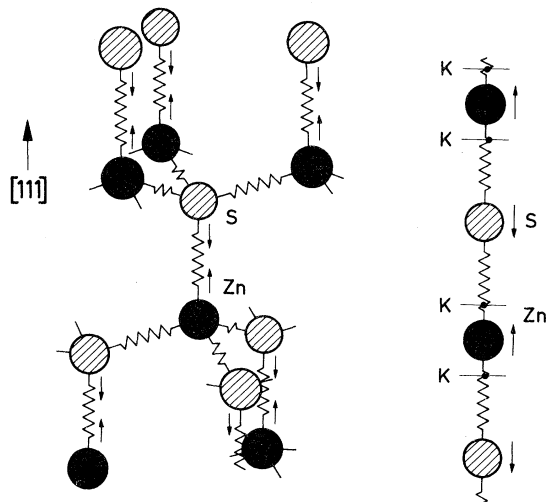

FIG. 3. The LO (L) phonon is a standing wave in [111] direction. The arrows indicate the displacement of the ions. The lattice vibration can be replaced by a linear chain vibration. K indicates the nodes of the vibration.

nodes of the vibration are the centers of gravity of neighboring vibrations. The forces acting on a Zn ion result from the four bindings to sulfur ions. In the model they are replaced by springs bound to the ions which are treated as simple points of mass. Nothing else has to be known except the spring constants for a displacement in [111] direction. The forces resulting from the three sulfur ions in $[1\,\overline{1}\,\overline{1}]$, $[\overline{1}\,1\,\overline{1}]$ and $[\overline{1}\,\overline{1}\,1]$ direction (see Fig. 3) are decomposed in components parallel and perpendicular to the [111] direction. For small displacement the perpendicular components stay unchanged and only the [111] components have to be taken into account. The sum of these forces has to be the same as, but of opposite sign to, the force of the [111] bond, because on the average the Zn ion is in the equilibrium position at small amplitudes. Similar considerations apply to the S ions with their four Zn-ion neighbors. By this the motion of a Zn ion in a LO (L) phonon mode is mapped into a mirror-symmetric arrangement of a Zn ion and two springs with spring constants $D_3/2$ and a resonance frequency of

$$W_{LO} = (D_3/M_{Zn})^{-1/2} = \Delta_3$$

$$= 338.6 \pm 0.3 \text{ cm}^{-1}.$$

W_{LO} is the LO phonon frequency, M_{Zn} the mass of the Zn ion, and D_3 is the spring constant for this vibration. Note that only nearest-neighbor forces are present. The elastic properties cannot be used for this calculation because they are furthermore influenced by long-range forces.

Next we describe the simplest local vibration of an M center. In any local mode each ion is displaced only in directions compatible with its size symmetry which is lower than at a regular lattice site. There are six ions around an M center with one nearest-neighbor vacancy and four around an F center. These ions normally vibrate toward and away from this vacancy. The most simple vibration is the breathing mode which is depicted in Fig. 4 for the M center. All ions move at the same time towards or away from the center. The vacancies are nodal points of the vibration. All ions vibrate at the same frequency and it is sufficient for the frequency calculation to determine only one other node. It is advantageous to select an ion with the most favorable symmetry properties. For the breathing mode this is one of the Zn ions with only one nearest-neighbor vacancy.

For the bonds to the S ions it is the same case as for the LO (L) phonon and in a good approximation the nodal point and spring constant $D_3/2$ obtained above can be used. At this point we neglect the difference in effective charge of vacancy and electron. The spring connecting the Zn ion and the vacancy is longer by a factor

$$d_2 = (M_{Zn} + M_S)/M_S$$

compared to the LO (L) phonon case. M_S is the mass of the S ion. The resulting spring constant is
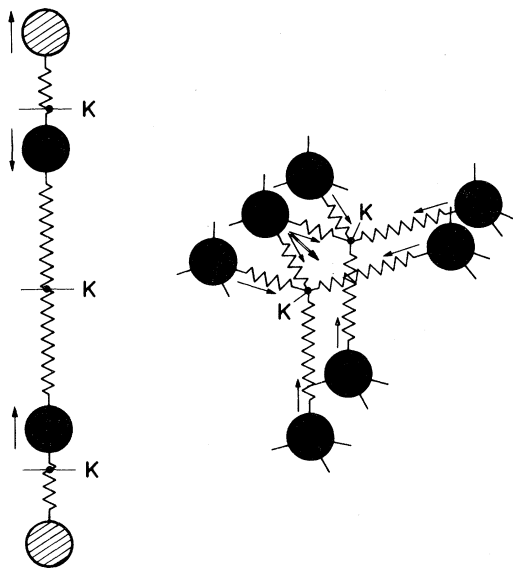

FIG. 4. The full symmetric mode of an M center. In ZnS this mode has a frequency of $\Delta_2 = 264$ cm^{-1}. It is an acoustical monopole mode. The equivalent linear chain is also depicted.

$$D_2 = D_3/2[I + M_S/(M_{Zn} + M_S)]$$

and the resonance frequency is

$$W_2 = \left[\frac{D_2}{M_{Zn}}\right]^{1/2} = W_3[\tfrac{1}{2} + M_S/2(M_S + M_{Zn})]^{1/2}$$

$$= 275 \text{ cm}^{-1}$$

already in fair agreement with the experimental value

$$\Delta_2 = 264.3 \pm 0.5 \text{ cm}^{-1} .$$

Actually the W_2 mode has a longer wavelength than W_{LO} and a correction has to be taken into account for the displacement of the nodal point away from the Zn ion. By assuming that this distance increases proportionally to $1/W_2^{(n-1)}$ as the wavelength in a continuum, and iterative approximation formula for the corrected frequency is derived,

$$W_2^{(n)} = W_3\left[\frac{1}{2} + \left[\frac{W_2^{(n-1)}}{W_3}\right]^2 \frac{M_S}{2(M_S + M_{Zn})}\right]^{-1/2} .$$

The calculated frequencies $W_2^{(1)} = 263.8$ cm^{-1} and $W_2^{(\infty)} = 261.5$ cm^{-1} are in excellent agreement with the observed value. This vibration is that of an acoustic monopole and would exibit strong radiation damping in a continuum. However, the resonance is in the gap between the optical and acoustical lattice phonons and the wave cannot expand into the crystal.

Another simple mode is similar to the breathing mode described before but with the Zn ions belonging to the different vacancies vibrating out of phase (see Fig. 5). Again the vacancies are nodal points. The Zn ion with both vacancies as nearest neighbors is the best to select for the description. It moves parallel to the line connecting the two vacancies. At small displacements the distance to the two S ions stays unchanged and the main repellent forces arise from the interaction with the vacancies. Their appropriate spring constant is D_2 derived above. The effective spring constant D_1 of this vibration is the sum of the two components parallel to the axis of displacement. This component can be calculated from the bond angles. The resonance frequency is

$$W_1 = (D_1/M_{Zn})^{1/2} = W_3(0.41/d_2)^{1/2}$$

$$= 124 \text{ cm}^{-1} .$$

Although this mode is insensitive to small local distortions not taken into account in this simple model, the agreement with the experimental value of

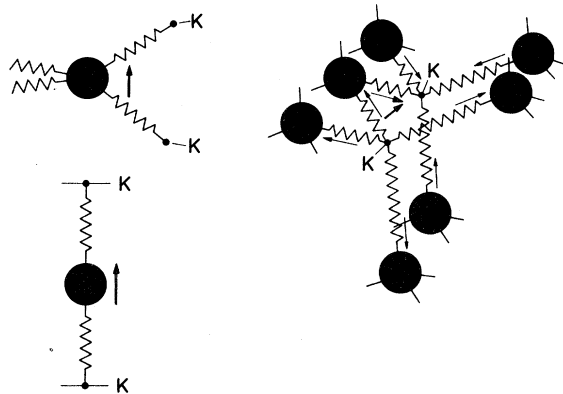$$\Delta_1 = 124.2 \pm 0.4 \text{ cm}^{-1}$$

FIG. 5. Out-of-phase vibration of the two groups of zinc ions. The frequency is $\Delta = 124$ cm^{-1} in ZnS—an acoustic dipole mode. The linear chain is an equivalent of this mode.

is surprisingly excellent. Radiation damping is small in this case, because it is an acoustic dipole.

The last mode treated is the dipole vibration depicted in Fig. 6. The movement is similar to the W_1 mode except for a Π phase change of the inner Zn ion. The vacancies are not nodal points for this mode. However, the mapping into a linear chain problem reveals that the nodal points are close to the outer Zn ions (see Fig. 6). Therefore, these Zn ions move with very small amplitude. In the approxima-
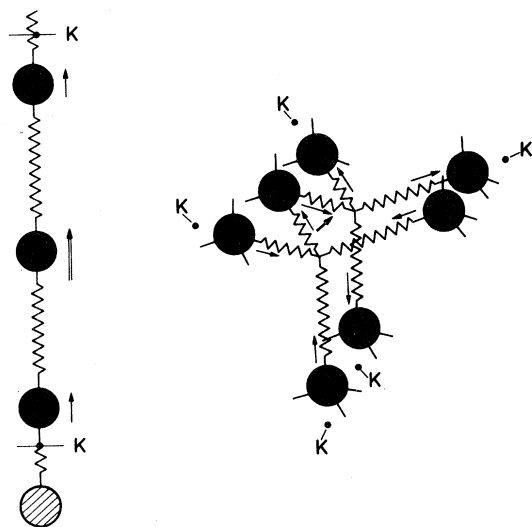

FIG. 6. Acoustic dipole vibration of the M center. The frequency is $\Delta_0 = 85.5$ cm^{-1} in ZnS. Note the large distance between the nodal points compared to the former modes.

tion of no movement, that is, where the Zn ions are modal points, the resonance frequency is given by

$$W_0 \leq W_1/\sqrt{2} = 87.5 \text{ cm}^{-1}$$

in good agreement with the experiment $(\Delta_0 = 85.5 \pm 1 \text{ cm}^{-1})$.

IV. THE M-CENTER EMISSION IN ZnS

The line structure of the M-center emission can be explained using the frequencies of the local vibrations of the M center obtained above. In the following the lines will be numbered according to Ref. 1 and Fig. 1. The spectrum consists of two parts: the lines 1–9 with energies higher than 11951 cm^{-1} and the lower-energy lines. The emission intensity of the first part varies for different crystals while the second part scales with the intensity of line 10 for all the crystals.[1]

A. The zero-phonon lines

All the experimental facts reported by Broser et al.[1] are consistent with the identification of the lines 10 and 11 as zero-phonon lines. The intensity scaling with line 10 shows that it is the highest-energy line of the normal M-center emission. Zeeman experiments[1] reveal that the ground state and the excited state of both lines are the same.

The intensities and energy differences of the phonon satellites strongly support the identification suggested. Line 11 has a three-times-higher emission intensity than line 10. This intensity ratio 3:1 is repeated in their low-energy phonon satellites with the phonons

$$\Delta_2 = 264.3 \pm 0.5 \text{ cm}^{-1}$$

and

$$\Delta_3 = 338.6 \pm 0.3 \text{ cm}^{-1} .$$

An explanation of line 11 as a phonon satellite of line 10 with phonon energy $\Delta_4 = 25.5 \pm 0.2$ cm^{-1} has to be ruled out. If the selection rule for the strongly forbidden triplet-singlet transition would be such that a transition with a vibration excitation would be stronger than the zero-phonon line itself, then the two or more phonon transitions should be of comparable strength. This was not observed.

Evidence for the origin of the two zero-phonon lines can be taken from their intensity ratio 3:1. A small [111] distortion of the M center at one of the four Zn-S binding directions would lead to two distinct types of M centers (Fig. 7) having different distances between the vacancies. The ratio of their statistical probability (in an isotropic crystal) is 3:1. Such a distortion is not unlikely. ZnS crystals can grow in (cubic) zinc blende or in (hexagonal) wurt-
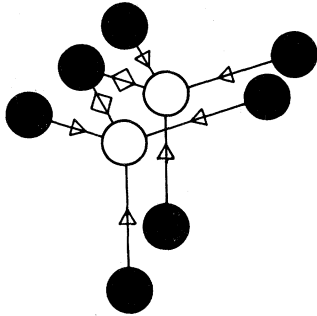
FIG. 7. The two different types of [111] of the M center. The mark indicates the possibilities of the one Zn—S bond with changed distance.

zite structures.

In cubic ZnS stacking faults are well known and are present in most crystals. In wurtzite-type ZnS one of the four S ions has a larger distance to the Zn ion than the others. This small distortion to lower symmetry splits the excited state. This fact has been discussed for the F center in ZnS.[4] Owing to the limited experimental sensitivity no such splitting was observed for the M center in Zeeman experiments.[1]

Using the Heitler-London and ϵ approximations an electronic model of the M center has been derived.[1] If a [111] distortion is assumed as the reason for the splitting of the two zero-phonon lines, the singlet-triplet energy difference $\Delta_4 = 25.5$ cm^{-1} can be used to determine the equivalent difference in distance in the Heitler-London approximation curve of the unbalanced H_2 molecule. It results in a reduced distance between the two vacancies of $\Delta = 9 \times 10^{-3}$ Å, while their distance is $r_0 = 3.8$ Å, i.e., $\Delta r / r = 2\%$. This proposed [111] distortion is large enough to obtain final proof from future EPR experiments.

B. The phonon satellites

The energies of most of the spectral features of the M-center emission can be explained by subtracting the vibrational energies $\Delta_0 - \Delta_3$ and their combinations from the zero-phonon lines 10 and 11. Some of the lines have already been assigned by Broser et al.[1] The coupling to the two zero-phonon lines varies for the different local modes. Line 21 $(10 + \Delta_1)$ and line 22 $(11 + \Delta_1)$ as well as lines 41 $(10 + \Delta_1 + \Delta_3)$ and 43 $(11 + \Delta_1 + \Delta_3)$ have nearly the same intensity while line 28 $(10 + 2\Delta_1)$ is stronger than line 30 $(11 + 2\Delta_1)$. Δ_0 shows strong coupling with line 11 to 20 $(11 + \Delta_0)$ to 24 $(11 + 2\Delta_0)$, but couples weakly with line 10 to 17 $(10 + \Delta_0)$ and to 23 $(10 + 2\Delta_0)$. Further low-energy satellites of lines

10 and 11 can be expected if further phonons exist. If additional ions vibrate in phase with the seven Zn neighbors the nodes are more distant and the frequencies are lower. Then the simple model fails because long-reaching forces cannot be neglected anymore. The radiation damping of such vibrations is stronger than that for the extremely localized vibrations discussed above and the lines are broadened. In the region between lines 11 and 20 only the relative strength of line 14 is striking. One possible explanation for this line is that it results from a change in the optical transition from an excited state with lower energy to the ground state in a more distorted configuration. Furthermore, lines 15 and 18 could be phonon satellites to this transition.

C. The high-energy satellites

An assignment of the high-energy satellites (lines 1—9) is proposed to M centers near crystal defects like polytype structures and to interaction of M centers. This is in agreement with the fact that their intensities vary from crystal to crystal. The local vibration of one M center can be absorbed resonantly by others. The decay of an excited and vibrating center can lead to high-energy satellites by annihilation of this vibration. The coupling of the centers is influenced by their density and the crystal quality; therefore it varies for different crystals.

V. CONCLUSION

In this paper I present a simple spring and mass model for the calculation of the main local vibrations of an M center and use the results to reinterpret the M-center emission of ZnS. The description is based on an intuitive anticipation of the fundamental vibrations of the center. The model can keep simple because the static displacement of the surrounding ions from their perfect lattice position is small. For each of the vibrations the nodes closest to the M center were determined and the surrounding region replaced by a fixed wall. The spring constants belonging to the respective vibrations were derived from the spring constant for the Zn—S bond stretching which can be obtained from the LO (L) phonon frequency by elementary considerations. Three fundamental modes were identified and their frequencies calculated. The results are in very good agreement with the frequencies observed experimentally for ZnS.

Using those local mode frequencies and the LO (L) phonon frequency the M-center emission of ZnS was interpreted. The result strongly suggests that the emission originates from two zero-phonon lines. Almost all of the other pronounced lines can be explained as one or several phonon satellites to these

zero-phonon lines. A small [111] distortion of the M center is proposed as the mechanism producing two zero-phonon lines. Two distinct distortions are possible with a statistical probability 3:1, in agreement with the emission intensity of the two lines. The energy difference of the two lines is used to estimate the difference in distance of the two types of [111] distortions within the frame of the Heitler-London and ϵ approximations. The difference of 2% is too small a change to be observed by the Zeeman experiments of Broser et al.[1] The higher-energy satellites of the two zero-phonon lines are attributed to M centers near crystal defects and to interaction of M centers, because their intensity varies for different crystals. For the remaining pronounced phonon satellite feature an optical transition is proposed which is accompanied by a change of the type of [111] distortion.

ACKNOWLEDGMENTS

[1]I. Broser, R. Germer, F. Seliger, and H.-J. Schulz, J. Phys. Chem. Solids 41, 101 (1980).

[2]P. Pêcheur, E. Kauffer, and M. Gerl, Phys. Rev. B 14, 4521 (1976).

[3]D. Wruck, Phys. Status Solidi B 48, 181 (1971).

[4]A. H. Harker, J. Phys. C 9, 3141 (1976).

[5]H. Bergsma, Phys. Lett. 32A, 324 (1979).

[6]N. Vagelatos, D. Wehe, and J. S. King, J. Chem. Phys. 60, 3613 (1974).

[7]M. Vandevyver and P. Plumelle, J. Phys. Chem. Solids 38, 765 (1977).

[8]Y. Kayanuma and Y. Toyozoawa, J. Phys. Soc. Jpn. 40, 355 (1976).

[9]Y. Kayanuma, J. Phys. Soc. Jpn. 40, 363 (1976).

[10]J. R. Townsend, Phys. Rev. B 14, 5535 (1976).

[11]Shi-yu Wu, J. A. Cocks, and V. Chin, Phys. Status Solidi B 83, 365 (1977).