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Edge Emission and Magneto-Optical Effects in CdSe

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More than a score of sharp, narrow, spectral lines (half-widths ~0.5 Å) have been observed in the edge-emission spectra of CdSe platelets. Several typical lines have been examined in detail at temperatures ~1°K. The spectral-line splittings of singlets, as well as zero-field-split doublets, have been studied in magnetic fields up to 45 000 G. The splitting of I_7 (an emission line appearing at 6827.43 Å) has been studied as a function of magnetic field strength. In accordance with the Thomas-Hopfield theory, arguments are presented for the association of I_7 with a bound-exciton complex; this line is observed to split linearly as a function of magnetic field strength and isotropically as a function of crystal orientation. Isotropic electron and hole g values have been determined for I_7: $g_e=0.50$ and $g_h=1.96$. A complex multiplet, $I_{9a}-I_{9b}$ (6855.14, 6857.35 Å), whose components split linearly and isotropically, has also been studied as a function of field strength. It is shown how the components of $I_{9a}-I_{9b}$ could arise from the excited states of a neutral exciton complex. Isotropic splittings were observed for all of the bound exciton lines; also, the electron g values were observed to be isotropic and essentially the same for all lines (about 0.50). Unlike CdS and ZnO, orientation-dependent Zeeman patterns were not observed in the CdSe spectra.

I. INTRODUCTION

IT is now over 25 years since Kroger[1] first reported a characteristic green luminescence from CdS, a luminescence which has generally come to be known as edge emission and is so called because of its spectral proximity to the optical-absorption edge; yet, in spite of a long history, the general subject of edge emission still seems to be capable of inspiring much new research in the Group II–VI materials, especially in single crystals. That the subject of edge emission still commands such a large following is not surprising. The continued interest is due, in no small measure, to the fact that much about the energy band and defect structure of these materials can still be learned from emission spectra. This fact is particularly true of the sharp, narrow, fluorescence lines that are observed very near to the onset of intrinsic absorption in wurtzite crystals from the II–VI group.

Although the existence of excitons in the II–VI compounds is well known, especially in the wurtzite crystals, it is perhaps less well known that the excitons of these materials fall generally into two categories: (1) the *intrinsic* or free exciton, existing as a hydrogenically bound, hole-electron pair, and (2) the *extrinsic* or bound-exciton complex, composed of a free exciton molecularly bound to a defect or "chemical center" in the host crystal. The intrinsic excitons are observed very near to the onset of intrinsic spectral absorption, as shown in Fig. 1, while the bound-exciton lines (for a given energy band) fall generally on the low-energy side of the intrinsic exciton lines. It is to this latter type of exciton that we shall address ourselves in the present report; in particular, we shall be concerned with the bound-exciton emission spectrum of CdSe.

Of the 12 chalcogenides of Zn, Cd, and Hg, most of which have been successfully synthesized as single crystals, only four normally crystallize in the hexagonal

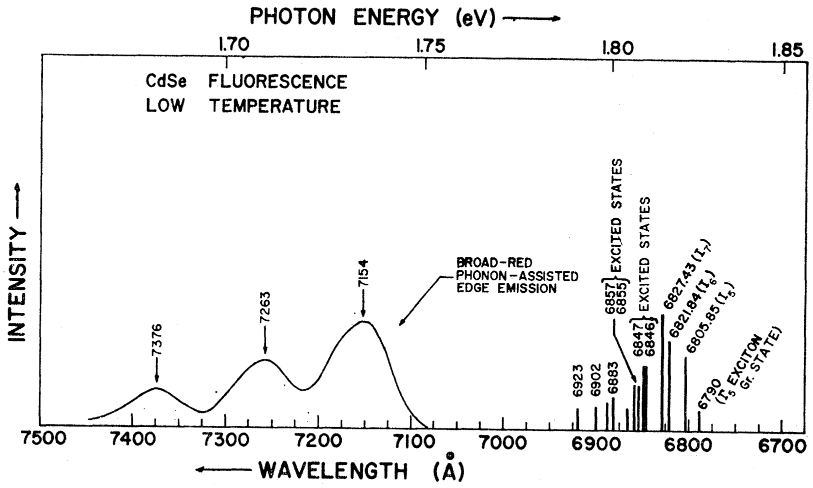

FIG. 1. Spectral diagram of some characteristic emission lines in CdSe crystals at 4.2°K and below. Lines are drawn to represent some of the sharp, narrow, fluorescent lines at the appropriate wavelengths. While intensities are generally represented by line heights, intensities are not meant to be quantatively comparable. I_4 is usually the most intense line in the CdSe emission spectrum but it is always accompanied by a rather intense background emission. All of the emission lines reported for CdSe are preferentially polarized in the mode $E\perp c$; however, the emission from CdSe is not nearly as strongly polarized as is the emission from CdS. The broad, red peaks at 7154, 7236, and 7376 Å are the phonon-assisted, edge-emission peaks and are analogous to the "green" peaks in CdS.

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[1] F. A. Kroger, Physica 7, 1 (1940).

modification (CdS, CdSe, ZnS, ZnO). Of the four wurtzite crystals, CdSe has received surprisingly little attention, especially with regard to its optical properties; the others, CdS, ZnS, and ZnO, have been the subject of considerable investigation over a period of many years.[2,3] On the other hand, the intrinsic exciton spectrum of CdSe has been examined rather thoroughly by Wheeler and Dimmock[4,5]; in particular, they have observed fine structure near the optical-absorption edge which arose from excited states of the pure crystal. From their study of intrinsic exciton structure, Wheeler and Dimmock deduced many of the energy-band parameters of CdSe, important among which were the exciton, hole, and electron effective masses. In a later paper, Sobolev[6] has also treated the exciton problem in CdSe, but his results were taken mostly from intrinsic absorption and reflection spectra. The intrinsic exciton parameters of the other wurtzite crystals have been previously reported: In a series of earlier papers on CdS and ZnO, Thomas and Hopfield[2,7–9] have given excellent and definitive treatments of the intrinsic exciton problem; more recently, Wheeler and Miklosz[10] have considered the intrinsic exciton structure of ZnS.

The first report of bound-exciton spectra in CdSe was made by Reynolds and Litton.[11] It is the purpose of the present paper to report the detailed results of this earlier work; to interpret the results in terms of the wurtzite band structure; and to discuss several of the extrinsic exciton lines in terms of specific bound-exciton complexes and their excited states. A summary of the CdSe emission lines that we have studied is given in Table I, together with several other extrinsic lines which appear in photoconductivity spectra.[12] We have studied the magnetic-field splittings of several of these lines in detail. More than a score of emission lines have been observed in the CdSe spectra; however, the lines I_1 through I_{14} represent a cross section of the different types of magnetic-field splittings that were observed.

The broad-band emission spectrum of CdSe, upon which phonon replicas of the bound-exciton lines are frequently superimposed, has been previously studied by several investigators and will not be considered here in detail. Keller and Pettit[13] were among the first to examine the broad-band fluorescence of CdSe and they observed that the emission at 77°K was slightly polarized in the mode $\mathbf{E}\perp c$. Broser and co-workers[14] have also examined the broad spectral emission of CdSe and have found two peaks at 4°K: one at 6800 and another at 7700 Å. The broad-band spectrum also contains the phonon-assisted emission peaks; these broad red peaks are separated by the longitudinal optical phonon energy (0.026 eV) and were first studied by Pedrotti[15] and later by Wardzynski *et al.*[16] Pedrotti[15] has examined the temperature dependence of the phonon-assisted emission peaks as the temperature ranged from 4.2 to 77°K and, more recently, Wojtowicz-Natanson and Zakrzewski[17] have made similar measurements on two peaks (one at 6800 and the other at 7100 Å) as the temperature ranged from 300 to 4.2°K. Wojtowicz-Natanson and Zakrzewski have also suggested a specific exciton-complex assignment for the 6800 Å peak. However, this assignment is premature since the spectral resolution obtained in their measurements is at least an order of magnitude too low to resolve many of the sharp exciton-complex lines in this region. The phonon-assisted peaks are shown in the emission spectrum of Fig. 1, where the peak wavelengths are those given by Pedrotti; also shown, for comparison, are several of the bound exciton lines.

II. EXPERIMENTAL

The crystals used in the present experiments were of the platelet type and were grown from the vapor phase by a method due to Reynolds and Greene.[18] In the II–VI compounds, for reasons which are imperfectly understood, platelet growth (very thin and flexible single crystals) tends to be limited to those materials that crystallize in the wurtzite rather than the zinc-blende structure.[19,20] It is also true that the platelets

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[2] References to some of the earlier work on optical properties are collected in a recent review: (a) D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Status Solidi **9**, 645 (1965); (b) **12**, 3 (1965).

[3] Some of the early work on ZnO is discussed in the review by G. Heiland, E. Mollwo, and F. Stockman, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 8.

[4] J. O. Dimmock and R. G. Wheeler J. Appl. Phys. Suppl. **32**, 2271 (1961).

[5] R. G. Wheeler and J. O. Dimmock, Phys. Rev. **125**, 1805 (1962).

[6] V. V. Sobolev, Dokl. Akad. Nauk SSSR **152**, 1342 (1964) [English trans.: Soviet Phys.—Doklady **8**, 996 (1964)].

[7] D. G. Thomas and J. J. Hopfield, Phys. Rev. **116**, 573 (1959).

[8] J. J. Hopfield and D. G. Thomas, Phys. Rev. **122**, 35 (1961).

[9] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960). See also J. J. Hopfield, *ibid.* **15**, 97 (1960). Another study of the intrinsic spectrum of ZnO has recently been made: Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966).

[10] R. G. Wheeler and J. C. Miklosz, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie, Paris, 1964), p. 873. See also Phys. Rev. **153**, 913 (1967).

[11] D. C. Reynolds and C. W. Litton, Bull. Am. Phys. Soc. **9**, 224 (1964).

[12] Y. S. Park and D. C. Reynolds, Phys. Rev. **132**, 2450 (1963).

[13] S. P. Keller and G. D. Pettit, Phys. Rev. **120**, 1974 (1960).

[14] I. Broser, R. Broser-Warminsky, G. Klipping, R. Rass, and H. J. Schulz, J. Phys. Chem. Solids **22**, 213 (1961).

[15] F. L. Pedrotti, Ph.D. thesis, University of Cincinnati, 1962 (unpublished). See also Ref. 2b, p. 35.

[16] W. Wardzyuski and B. Wojtowicz-Natanson, in *Proceedings of the International Symposium on Radiative Recombination in Semiconductors* (Dunod Cie., Paris, 1964), p. 287.

[17] B. Wojtowicz-Natanson and T. Zakrzewski, Phys. Status Solidi **11**, 873 (1965).

[18] For a review of the methods and problems of growing single crystals from these materials, see the article by D. C. Reynolds, in *The Art and Science of Growing Crystals*, edited by J. J. Gilman (John Wiley & Sons, Inc., New York, 1963), p. 62.

[19] A theory of platelet growth has recently been proposed for CdS by J. Chikawa and T. Nakayama, J. Appl. Phys. **35**, 2493 (1964).

[20] Recently, in crystal-growing experiments with ZnO, Y. S. Park and D. C. Reynolds [J. Appl. Phys. (to be published)] have shed some light on the problem of platelet growth in these materials. Apparently, the platelet formation has to do with an anisotropic growth rate of dislocation "loops" at crystal growth planes, among other things. See also J. S. DeWitt, Y. S. Park, and D. C. Reynolds, Bull. Am. Phys. Soc. **11**, 179 (1966).

Table I. A summary of the emission lines observed in CdSe, several of which are discussed in detail in the text. The emission lines I_1–I_{14} were observed with high spectral resolution at a temperature of 1.2°K. The lines I_B and $I_{1p}-I_{6p}$ were observed in photoconductivity spectral response curves by Park and Reynolds[a] but they did not study these lines in fluorescence. The line I_{1p} has been observed in emission and is identical to line I_7 in the present fluorescence measurements; also, the line I_B may be equivalent to the I_5 of the present work. The lines I_B and $I_{1p}-I_{6p}$ were observed at 4.2°K with relatively low spectral resolution; they are included here for completeness and to avoid subsequent confusion with the line nomenclature.

Line	Wavelength (Å)	Wave number (cm^{-1})	Energy (eV)	Preferential polarization	Intensity	Splitting	g value
I_1	6790.9_5	14725.5	1.8254	$\mathbf{E}\perp c$	Weak	Doublet	0.52
I_2	6792.6_0	14721.9	1.8250	$\mathbf{E}\perp c$	Weak	Doublet	0.52
I_3	6794.1_2	14718.6	1.8246	$\mathbf{E}\perp c$	Weak	Doublet	0.52
I_4	6804.1_8	14696.8	1.8219	$\mathbf{E}\perp c$	Very strong	Multiplet	···
I_5	6805.8_5	14693.0	1.8214	$\mathbf{E}\perp c$	Strong	Doublet	0.53
I_6	6821.8_4	14658.8	1.8172	$\mathbf{E}\perp c$	Strong	Doublet	0.53
I_7	6827.4_3	14646.8	1.8157	$\mathbf{E}\perp c$	Strong	Quartet	1.96/0.50
I_{8a}	6846.6_2	14605.8	1.8106	$\mathbf{E}\perp c$	Weak	Complex	
I_{8b}	6847.3_9	14604.1	1.8104	$\mathbf{E}\perp c$	Weak	Complex	
I_{9a}	6855.1_4	14587.6	1.8083	$\mathbf{E}\perp c$	Weak	Complex	
I_{9b}	6857.3_5	14582.9	1.8078	$\mathbf{E}\perp c$	Strong	Complex	
I_{10}	6868	14560	1.805	$\mathbf{E}\perp c$	Weak	Complex	
I_{11}	6883.8_2	14526.8	1.8008	$\mathbf{E}\perp c$	Weak	Quartet	1.9/0.50
I_{12}	6889	14520	1.799	$\mathbf{E}\perp c$	Weak		
I_{13}	6902	14490	1.796	$\mathbf{E}\perp c$	Weak		
I_{14}	6923	14450	1.791	$\mathbf{E}\perp c$	Weak		
I_B	6807	14691	1.821	$\mathbf{E}\parallel c$			
I_{1p}	6827	14650	1.816	$\mathbf{E}\perp c$			
I_{2p}	6783	14740	1.828	$\mathbf{E}\perp c$			
I_{3p}	6774	14760	1.830	$\mathbf{E}\parallel c$			
I_{4p}	6764	14780	1.833	$\mathbf{E}\perp c$			
I_{5p}	6729	14860	1.842	$\mathbf{E}\parallel c$			
I_{6p}	6721	14880	1.844	$\mathbf{E}\parallel c$			

[a] See Ref. 12.

(and hence the wurtzite structure) are the best crystals for most optical measurements, since they are of sufficiently high purity and structural quality to permit detailed studies of the spectral fine-structure near the absorption edge.

The platelet samples ranged in thickness from 0.5 to 50 μ and were glued on one end (relatively strain free) to a sample holder which was in turn placed in the tip of a glass helium Dewar. The mounting was arranged so that the samples were immersed in liquid He. Provision was made for pumping on the liquid He and the temperature was measured by means of vapor-pressure thermometry, using an oil manometer. All of the experiments were conducted at approximately 1.2°K. The Dewar tip was inserted in the air gap of a conventional dc electromagnet, the pole tips of which were separated by $\frac{5}{16}$ in. The maximum magnetic field strength of this magnet was 45 000 G and this was the greatest field strength used in any of the experiments. A 500-W Hg lamp (Osram high pressure), equipped with a *blue filter*, was used for fluorescence excitation. Spectral analysis of the crystal emission was made with a Bausch and Lomb 2-m grating spectrograph. The spectrograph employed a large, high resolution, diffraction grating and produced a reciprocal dispersion of approximately 2 Å/mm in first order. With this grating, the spectrographic aperture was about $f/16$. The spectral resolution ranged from about 0.02 to 0.4 Å (as can be seen from the magnetic data, many of the weak lines are resolved and are split by less than 0.5 cm^{-1}, or 5×10^{-5} eV). All of the spectra were photographically recorded on Kodak type IN spectroscopic plates.

III. RESULTS AND DISCUSSION

A. Exciton Complex Models

A mathematical model for bound-exciton complexes was first discussed in a paper by Lampert[21] who referred to such particle aggregates as "effective-mass-particle complexes." Such complexes were first observed by Haynes[22] in the absorption spectra of silicon crystals. As used here, "bound-exciton-complex" refers to an intrinsic exciton bound to a chemical defect, where the chemical defect can derive from either an impurity atom or host lattice defect and can assume the form of a neutral or ionized donor or acceptor in the semiconductor (the bound excitons are sometimes referred to as "impurity" excitons). In addition to their work on intrinsic exciton spectra, Thomas and Hopfield[23,24] also

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[21] M. A. Lampert, Phys. Rev. Letters **1**, 450 (1958).

[22] J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).

[23] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962). See also D. G. Thomas and J. J. Hopfield, Phys Rev. Letters **7**, 316 (1961).

[24] J. J. Hopfield, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 725.

investigated bound excitons in CdS and were successful in identifying a number of absorption and emission lines[25] with specific complexes; they also worked out a theory of bound excitons, based upon the wurtzite structure of CdS. In their treatment, only the lowest states of the complexes were considered and the model was one in which the complex was bound together by forces similar to those in the hydrogen molecule or the hydrogen-molecule ion. They also considered the perturbing effect of an applied magnetic field on the optical transitions from such complexes in CdS. Since CdSe is a similar type of compound, with the same crystal structure, one would expect the magneto-optical effects arising from bound-exciton transitions to be very similar to those observed in CdS. However, significant differences have been observed between the magneto-optical effects of these two materials. The most outstanding difference is the fact that, in magnetic fields up to 45 000 G, essentially isotropic spectral-line splittings are observed in the CdSe fluorescence whereas considerable anisotropy is observed in CdS. Also, optical transitions which appear to involve excited states of bound-exciton complexes have been observed in the CdSe spectra, as we shall show in the present report. Thomas and Hopfield[23] have predicted the observation of excited states in the optical transitions of these materials; moreover, they have observed emission lines in CdS characterized by large magnetic-field splittings and negative diamagnetic shifts and have attributed such spectral lines to excited states of an exciton complex.

The energy-level schematics and Zeeman patterns of several bound-exciton-complex models are shown in Fig. 2. These exciton models derive from the Thomas-Hopfield theory and were first applied to CdS; they should, of course, apply to any of the wurtzite crystals. The symbols $\oplus$ and $\ominus$ represent ionized donors and acceptors, respectively, and the $+$ and $-$ represent holes and electrons. The holes used in the formation of these complexes originate from the top valence band which has Γ_9 symmetry at $\mathbf{k}=0$. I_0 represents the intensity of a single line of a given type for zero magnetic field strength; θ is the angle between the crystalline c axis and the direction of the magnetic field; and H represents the magnetic field strength. The symbols g_e and g_h represent the electron and hole g values, respectively, while the symbol Δ represents the splitting between Γ_5 and Γ_6 exciton states, arising from spin-spin exchange interaction. In the present meaning, the expression "Γ_6 exciton" (or "Γ_5 exciton") refers mainly to bound-exciton states; in particular, it refers to ionized complex states formed from the binding of an intrinsic exciton to an ionized donor or acceptor, where the intrinsic exciton can be in either a Γ_5 or a Γ_6 state. We recall that an intrinsic exciton in a Γ_6 state is one whose hole and electron spins are parallel, while the spins are antiparallel for an exciton in a Γ_5 state.

The spectral transitions which arise from an intrinsic exciton bound to either a neutral donor, or a neutral acceptor are shown in Figs. 2(a) and 2(b), respectively. Such complexes are characterized by states which split linearly in a magnetic field. Similar transitions for an exciton bound to a charged donor or acceptor are shown in Fig. 2(c); however, the magnetic splittings of the ionized complexes are nonlinear functions of both crystal orientation ($\cos\theta$) and field strength (H). For the case where the crystal is oriented with $c\perp\mathbf{H}$, it can be seen from the diagrams 2(a) and 2(b) that the hole spin does not split. This property of the neutral complexes gives rise to a low-temperature thermalization of states which, in turn, gives rise to predictable variations in line intensities; these intensity variations frequently permit the identification of specific lines with specific bound-exciton complexes. Thermalization effects have been demonstrated for several lines in CdS[23,26]. On the other hand, thermalization effects are not generally expected from the ionized complexes. On purely theoretical grounds, transitions from the Γ_6 state are forbidden in zero magnetic field [see Fig. 2(c)]. Moreover the Γ_6 transitions are not observed in the absorption spectra of CdS [23]; however, in the fluorescence spectra, these transitions are observed for both the bound and intrinsic excitons.[26,27] The theoretical models predict that the bound-exciton spectral lines will be *anisotropically* split in magnetic fields of arbitrary strength, a prediction which is supported by experiment in CdS[23,26] and ZnO.[28] Both linear and nonlinear magnetic-field splittings are observed in CdSe, but, as we shall show, all of the spectral lines are essentially isotropically split in a magnetic field of fixed intensity.

B. Lines I_5 and I_6

The emission line I_6 (6821.84 Å) is a strong line that splits into a doublet in a magnetic field. The splitting of I_6 is shown in Fig. 3, where the photon energies of its split components (in units of cm^{-1}) are plotted as a function of magnetic field strength, with the cyrstalline c axis oriented parallel to the direction of the magnetic field ($c\|\mathbf{H}$). When the square of splitting of I_6 is plotted as a function of the square of the magnetic field strength, a linear relation obtains, as shown in Fig. 4. (In this case, the splitting ΔE is the energy of separation of the split components of the doublet in units of eV). The

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[25] While some of the exciton lines in the II–VI materials are observed in both absorption and emission spectra, most of the bound-exciton lines are observed only in fluorescence; on the other hand, a few of the bound-exciton lines are observed only in absorption. In this connection, CdSe is certainly no exception.

[26] D. C. Reynolds and C. W. Litton, Phys. Rev. **132**, 1023 (1963).

[27] D. C. Reynolds, C. W. Litton, and R. G. Wheeler, in *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie., Paris, 1964), p. 739.

[28] D. C. Reynolds, C. W. Litton, and T. C. Collins, Phys. Rev. **140**, A1726 (1965).

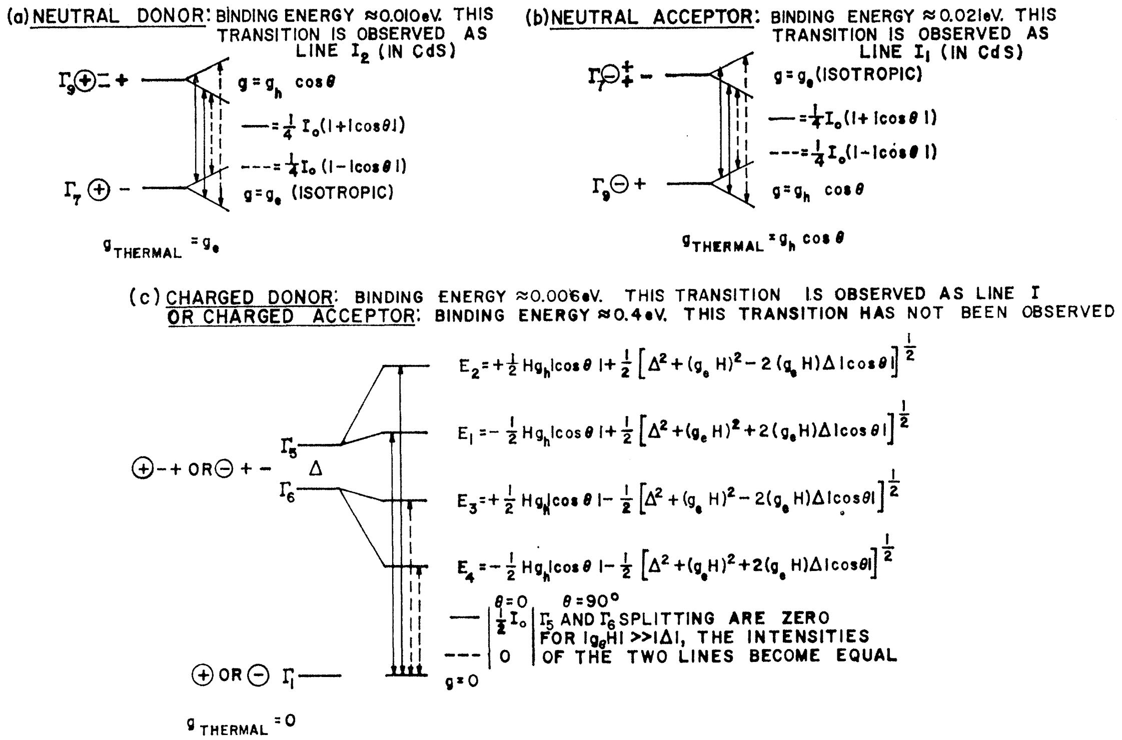

FIG. 2. A schematic representation of the energy levels of complexes which can be formed using holes only from the top valence band. In (a) and (b) linear splittings are observed, but in (c) the splittings are more complex and the energy levels are given. The expressions associated with the dashed or solid lines refer to the intensities of the transitions. θ is the angle between the crystalline c-axis and the direction of the magnetic field. (After Thomas and Hopfield.)

slope of $(\Delta E)^2$ versus H^2, together with the relation $\Delta E = g\beta H$, yields an effective g factor for the line I_6: $\text{slope} = (\Delta E)^2/H^2 = g^2\beta^2 = 9.25 \times 10^{-12}$, where β is the Bohr magneton; hence, we find that $g = 0.53$. This g factor is in good agreement with the electron g factor previously obtained in intrinsic exciton measurements.[4,5] A distinct diamagnetic shift is also observed in the split components of I_6, i.e., the center of gravity of the split pair shifts to higher energies with increasing magnetic field. For I_6, ΔE does not vary appreciably with θ at constant magnetic fields; hence, we say that an essentially isotropic splitting is observed for this line. Moreover, since the line splits as a doublet, it is likely that its terminal state is a singlet. This fact tends to indicate that I_6 arises from an exciton bound to an ionized center. In this case, however, the lower-energy component [Γ_6 state as shown in Fig. 2(c)] appears to be missing, even in the presence of a magnetic field. The binding energy of the complex is approximately 0.008 eV and is taken as the energy below the ground state of exciton A (6790 Å). Since the binding energy is small, the most logical assignment for I_6 is that of an exciton bound to an ionized donor. If the ionized donor

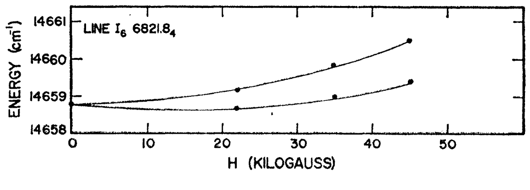

FIG. 3. A plot of the doublet components of the line I_6 at 1.2°K as a function of magnetic field strength, showing the splitting of this line for the orientation $c \| \mathbf{H}$.

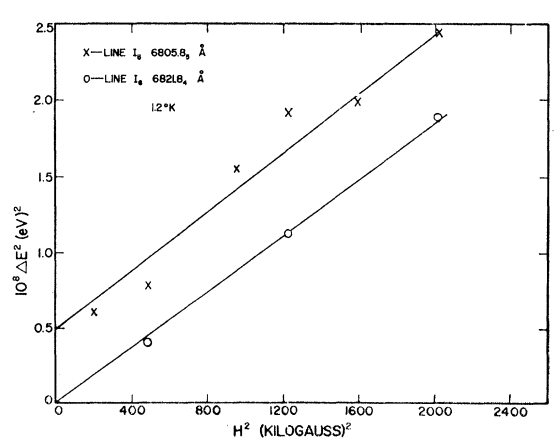

FIG. 4. $(\Delta E)^2$ is plotted as a function of H^2 for the lines I_5 and I_6, using the data of Figs. 3 and 5, where ΔE is the energy of separation of the doublet components of either I_5 or I_6 and H is the magnetic field strength.

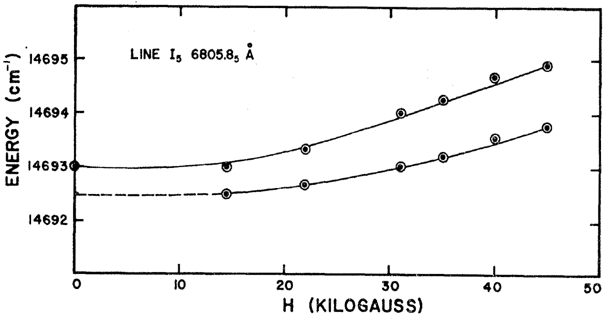

FIG. 5. Splitting of the doublet line I_5 at 1.2°K as a function of magnetic field strength for the orientation $c\|\mathbf{H}$. The lower dashed curve is an extrapolation of the low-energy component of I_5 back to zero magnetic field.

assignment is assumed, then I_6 is analogous to the I_3 line[23,26] of CdS. Unlike the I_3 line of CdS, however, the I_6 line of CdSe does not show a zero-field splitting.

The line I_5 (6805.85 Å) is another strong line that also splits as a doublet. The splitting of this line as a function of magnetic field strength is shown in Fig. 5, where the crystal is again oriented with $c\|\mathbf{H}$. For I_5 a zero-field splitting is indicated by extrapolation to $H=0$, but the low-energy component is not actually observed at fields below 15 000 G. In Fig. 4, we have plotted $(\Delta E)^2$ as a function of H^2 for the I_5 line (denoted by the x points); on the same graph, we have also plotted the data for the I_6 line (denoted by the o points). It is interesting to note that, within experimental error, the slopes of the plots for I_5 and I_6 are equal. This indicates that the effective g factors are the same for both of these lines, namely, $g_e=0.53$. Unlike the I_6 line, however, the linear plot for I_5 does not pass through zero, indicating that I_5 is zero-field-split by approximately 7×10^{-5} eV. In comparison with I_6, the magnetic splitting of I_5 is even more similar to that of the I_3 line in CdS[23,26]; moreover, the zero-field splitting of I_5 is directly analogous to the Δ splitting which separates the Γ_5 and Γ_6 exciton states, as shown in Fig. 2(c). In particular, the low-energy component of I_5 may be ascribed to a Γ_6 exciton transition which is forbidden in the absence of a magnetic field. In the presence of a magnetic field, however, the Γ_5 and Γ_6 states become mixed and the Γ_6 transition is allowed. As pointed out in Sec. III A, the zero-field splitting results from the spin-spin exchange interaction of an unpaired electron and hole. Like the I_6 line, I_5 also shows an essentially isotropic splitting. The isotropic splitting of I_5 is demonstrated in Fig. 6, where the photon energies of its split components are plotted as a function of crystal orientation (θ) while the magnetic field is held constant at 45 000 G. In Fig. 6, the center of gravity of the doublet is plotted at the zero-field position of I_5. Actually there is a slight upward shift in energy of the doublet centers of gravity as the crystal is rotated from $\theta=90°$ to $\theta=0°$, but there is a constant separation between the doublets throughout the range of θ.

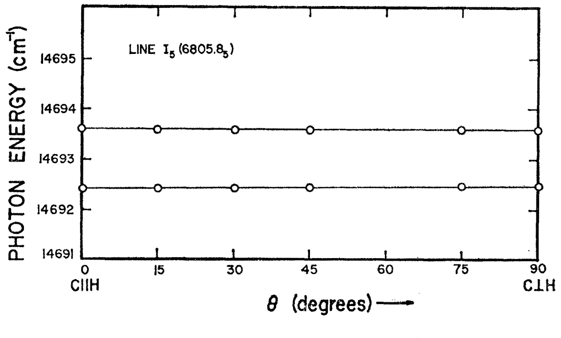

FIG. 6. Splitting of the emission line I_5 as a function of cosθ in a field of 45 000 G at 1.2°K. Here, as in Fig. 9, θ is the angle between the crystalline c axis and the direction of the magnetic field.

As in the case of I_6, the magnetic splitting of I_5 tends to suggest that this line also arises from an exciton bound to an ionized center. The fact that it splits as a doublet indicates a singlet terminal state. The zero-field splitting can also be accounted for on the basis of an exchange splitting in the upper state. The small ionization energy (0.004) eV again suggests that the exciton complex associated with I_5 is of the ionized donor type. While the isotropically split I_5 and I_6 lines remain a puzzle, they are not unique in CdSe; in fact, all of the emission lines listed in Table I show essentially isotropic splittings in magnetic fields up to 45 000 G.

C. Line I_7 (6827.43 Å)

The line I_7 is a strong line that splits into a quartet in a magnetic field. The behavior of this line in a magnetic field is shown in Fig. 7, where we have plotted its splitting as a function of magnetic field strength for the orientation $c\|\mathbf{H}$. I_7 is characterized by both linear (ΔE versus H) and isotropic (ΔE versus θ) splittings. Since the splitting of I_7 is linear and it splits as a quartet, it is likely that this line arises from a neutral complex. Ordinarily, as Thomas and Hopfield have shown,[23] the hole and electron g values of neutral complexes obey the relation

$$g=g_e\pm g_h=g_{e0}\pm g_{h\|}\cos\theta, \tag{1}$$

where g_e and g_h are electron and hole g values, respectively; g_{e0} is the isotropic g value of the electron; $g_{h\|}$ is the g value of the hole when $c\|\mathbf{H}$; and θ is, as usual, the angle between c axis and the direction of $\mathbf{H}$. In the case of I_7, however, Eq. (1) does not directly lend itself to the calculation of hole and electron g values, mainly because of the isotropic splittings of this line. In order to circumvent this problem, we have assumed that the small splittings in Fig. 7 are due to electron-spin splittings and that the large splitting is due to the hole-spin splitting. On the basis of these assumptions, we have calculated the following hole and electron g values for I_7: $g_h=1.96$ and $g_e=0.50$. The electron g value is

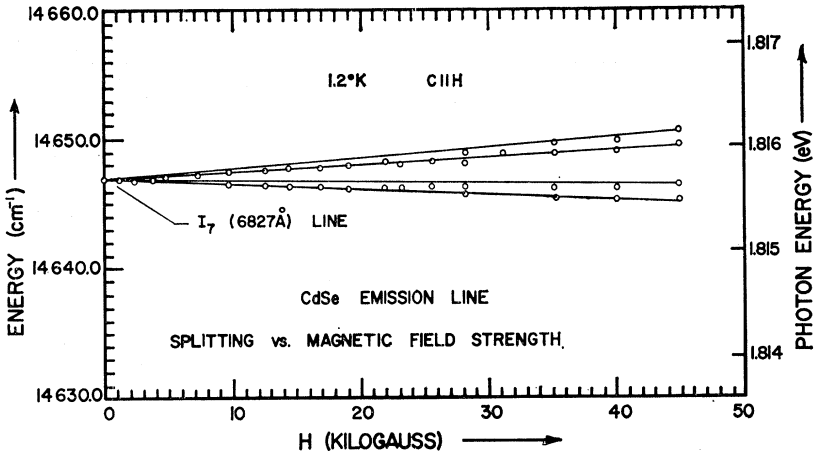

FIG. 7. Splitting of the quartet line I_7 at 1.2°K as a function of magnetic field strength for the orientation $c\|\mathbf{H}$.

nearly the same as the g values observed for the lines I_5 and I_6; it also compares very well with the g values obtained from intrinsic measurements. Wheeler and Dimmock[4,5] have obtained the following electron g values from the intrinsic exciton spectra of CdSe: $g_x=0.51\pm0.50$ and $g_z=0.6\pm0.1$. Thus, it seems likely that the small splittings in Fig. 7 arise from electron-spin splitting and our assumption is reasonable. Our assumption that the larger splittings arose from hole-spin splittings also appears to have been valid, since a hole g value of 1.96 is reasonable for these materials. As a consequence of the linear splitting, it seems reasonable to attribute I_7 to an exciton bound to a neutral center; however, we can offer no plausible explanation for the isotropic nature of the splitting. Thermalization effects were not observed in this line but the small binding energy (approx. 0.01. eV) suggests that it arises from a donor center. Another line, I_{11}, whose splitting is almost identical to that of I_7, was also observed. For I_{11} we have calculated the following g values; $g_e=0.50$ and $g_h=1.9$ The isotropic splittings of these lines, as well as those of the I_5 and I_6 lines, are distinctly different from most of the line splittings observed in CdS [23,26] and ZnO.[28] It should be pointed out, however, that at least one emission line in CdS is characterized by an isotropic splitting, namely, the I_6 line.[26]

D. Excited States of Exciton Complexes

A group of four lines are observed in zero magnetic field at the following wavelengths: 6846.62, 6847.39, 6855.14, and 6857.35 Å.They are denoted as I_{8a}, I_{8b}, I_{9a}, and I_{9b}, respectively. From the spectra one can not determine whether each line results from a separate exciton complex, or whether the lines arise from two complexes with I_{8a} and I_{8b} belonging to one complex and the last pair (I_{9a} and I_{9b}) being formed from another complex. In the later case, the small separation between I_{8a} and I_{8b}, as well as that between I_{9a} and I_{9b}, is a zero-field splitting caused by an exchange-energy term The magnetic-field splittings of these lines are given as a function of the magnetic field strength in Fig. 8. If attention is focused on the I_{9a} and I_{9b} pair (low-energy pair), one observes that they appear to have a negative diamagnetic shift and the magnitude of the splittings is large compared with what one would expect from a ground-state effective g value for a hole or electron. Similar observations as those found above in CdSe have been reported for CdS by Thomas and Hopfield; they

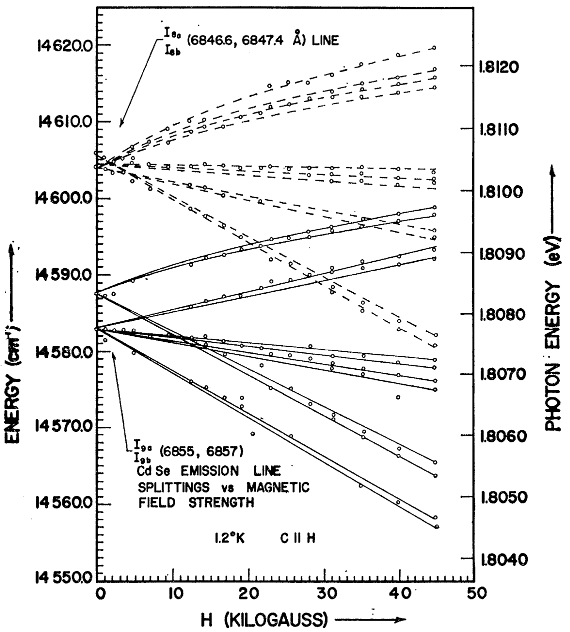

FIG. 8. Energies of the excited states of the bound-exciton lines I_8 and I_9 as a function of magnetic field strength with the crystal at 1.2°K in the orientation $c\|\mathbf{H}$. The I_9 line system is composed of two lines at $H=0$: I_{9a} (6855 Å) and I_{9b} (6857 Å). Similarly, it appears that the rather complex I_8 system goes into two lines at $H=0$, namely, I_{8a} (6846.6 Å) and I_{8b} (6847.4 Å). The I_{8a}, I_{8b} system is indicated by the dashed curves, while the I_{9a}, I_{9b} system is indicated by the solid lines.

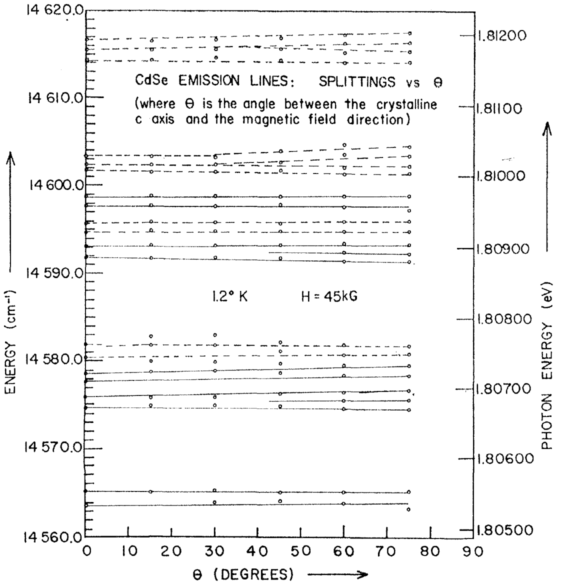

FIG. 9. Splitting of the emission line system I_{8a}, I_{8b}, and I_{9a}, I_{9b} as a function of cosθ with the crystal in a field of 45 000 G at 1.2°K. The line energies at $\theta=0°$ ($c\|\mathbf{H}$) correspond to the line energies at 45 000 G in Fig. 8.

tentatively attributed their observation to excited states of exciton complexes.[23]

Consider first only the low-energy components of these excited-state transitions, i.e., the I_{9b} line. When the magnetic field is turned on, I_{9b} splits into four sets of doublets as shown in Fig. 8. The two outside sets of doublets are separated by 4.4×10^{-3} eV at 45 000 G while the two inside sets of doublets are separated by about 4×10^{-4} eV at the same field strength. The small splittings which are superimposed on the large splittings have an energy difference of about 1.5×10^{-4} eV at this field. One can explain some of the above properties with the following model: Suppose that a neutral center traps an exciton (the exciton being in the $n=1$ state) and when the exciton decays it leaves the center in an excited state, namely, the $n=2$ state of the neutral complex (donor or acceptor). The effective particle mass calculated from this model is $\sim$0.1 m which is approximately the same as the mass of the electron found by Wheeler and Dimmock[4] for CdSe. The g value for the particle has a magnitude of 1.4. In this model the exciton and the bound particle would have to combine to give an effective g value of 0.5 for the upper state in order to account for the small splittings. Further, the difference between the I_{9a} and I_{9b} would arise from the energy difference of the Γ_5 and Γ_6 state of the exciton.

The I_{8a} and I_{8b} lines are not nearly so clearly defined as those of the I_{9a}, I_{9b} group, as can be seen from Fig. 8. From the splittings of the $I_{8a,b}$ group, one again observes small splittings which correspond to a g factor of $\sim$0.5 and large splittings which are associated with $n=2$ orbital motion of the effective particle.

The orientation dependence of the splittings of both the I_8 and I_9 groups is shown in Fig. 9, where the crystal was rotated from $\theta=0°$ to 75° and the magnetic field was held constant at 45 000 G. There is one to one correspondence between the splittings at 45 000 G in Fig. 8 and the splittings at $c\|\mathbf{H}(\theta=0°)$ in Fig. 9. (Here the lower-energy doublet of lines I_{9b} is not shown in this plot as it is weak and difficult to observe as the crystal is rotated.) As in Fig. 8, the dashed curves represent the I_8 complex, while the solid curves represent the I_9 line. In Fig. 9, one notes that each of the two sets of triplets (dashed curves observed at $\theta=0°$) separate into two sets of doublets at $\theta=45°$. Also, two sets of doublets (solid curves) separate into triplets at approximately the same angle ($\theta=45°$). One further observation and the most striking feature of the splittings is the fact that they are approximately isotropic.

IV. CONCLUSIONS

A systematic study has been made of the sharp, narrow emission lines which occur near to the onset of intrinsic absorption in CdSe at low temperatures. It has been shown that these lines arise from bound-exciton complexes and that they can be tentatively assigned, on the basis of magnetic-field splittings, to neutral or ionized exciton complexes. Unlike the Zeeman splittings of CdS[23,26] and ZnO,[28] however, all of the CdSe lines showed essentially isotropic splittings. In fact, normal Zeeman patterns were not observed in the CdSe spectra. The isotropic line splittings of CdSe

TABLE II. Typical bound-exciton parameters for several of the CdSe lines discussed in the text.

Line	Type of magnetic splitting	Exciton complex	Energy below exciton A (eV)	g_e (g value of electron, isotropic)	g_h (g value of hole, isotropic)
I_7	Linear, isotropic	Probably a neutral donor	0.01	0.50	1.96
I_{11}	Linear, isotropic	Neutral donor or acceptor	0.02	0.50	1.9
I_6	Nonlinear, isotropic	Ionized donor or acceptor	0.008	0.53	
I_5	Nonlinear, isotropic, and zero-field-split	Ionized donor or acceptor	0.004	0.53	
I_{9a}, I_{9b}	Complex multiplet, linear and isotropic	Neutral complex in excited states (possibly a neutral acceptor).		0.50	

remains a puzzle, since all of the splittings should be anisotropic. In many respects, however, the CdSe lines were similar to those of CdS and ZnO, as can be seen from the typical line complexes of Table II. Not unlike CdS, the CdSe complex lines also showed both linear and nonlinear magnetic splittings, as well as zero-field-split pairs and isotropic electron *g* values. Several of the linearly split lines undoubtedly arose from neutral complexes, but thermalization effects were not observed in the split components of these lines; consequently, it was not possible to determine, in the usual way, whether the neutral complex was of donor or acceptor origin. The excited states of a bound-exciton complex were rather dramatically demonstrated in the magnetic splittings of the line group, $I_{9a}-I_{9b}$. Since diamagnetic shifts are observed in intrinsic exciton spectra,[4] and since such shifts are to be expected from theory,[4,23] the observed negative diamagnetic shift in the spectral splitting of I_9 serves as further confirmation of excited states in this bound-exciton complex.

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Electron and Phonon Bound States and Scattering Resonances for Extended Defects in Crystals

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By making use of the translational symmetry associated with line and plane defects in crystals, we define certain subbands of the unperturbed electron and phonon bands. Certain Wannier functions and Green's functions associated with these subbands are defined and are used to study the existence of localized electron and phonon states and scattering resonances associated with extended defects. By firstly considering very simple examples of such perturbations, of arbitrary strength and secondly considering perturbations of quite general form but of small strength, we establish the general existence of electron and phonon bound states for line and plane defects, and the existence of electron and phonon scattering resonances for line defects. The effects of different characteristics of the unperturbed band structure are indicated. In contrast to the above results, bound states for point defects and scattering resonances for point and plane defects do not occur unless the perturbation exceeds a certain minimum strength. Our results underline the basic importance of including the band structure in scattering problems of this type and also the dangers of relying on perturbation approaches. Attempts which have been made to arrive at properties of crystal defects by the study of one dimensional models should also be reviewed in the light of our results. The above-mentioned bound levels form continuous bands which may lie partly between or within the allowed bands of the unperturbed crystal, and those electron levels that lie in the forbidden regions should have an important influence on the properties of semiconductors and insulators. Such effects have long been observed, and have been interpreted usually in terms of the "dangling bond" theory of Shockley and Read; our theory gives a much more general basis for their existence and, although the difficulties are considerable, seems to offer a means of quantitative investigation which previously did not exist. The electron and phonon scattering resonances seem to afford a natural explanation of the long-standing discrepancy between theory and experiment on the subject of dislocation contributions to electrical and thermal resistivities.

I. INTRODUCTION

THE problem of the scattering of conduction electrons in metals by localized point imperfections, using the Wannier-function–Green's-function technique of Koster and Slater[1] has been treated by several authors on the basis of simplified models, and has been discussed by Seeger[2] and Callaway,[3] who give further references. For our purposes, the important point to emerge from this work is that a localized point perturbation can give rise to neither bound states nor scattering resonances[4] in the electron spectrum unless its strength exceeds a certain value. Similar techniques have also been applied by several authors to the problem of phonon scattering by point defects, and Callaway[3] gives appropriate references. Again we find the perturbation must exceed a certain minimum strength in order to give rise to either bound states or scattering resonances in the phonon spectrum.

In this paper we adapt these methods to the study of electron and phonon scattering from line and surface defects which preserve the crystal periodicity in one and two dimensions, respectively. In Sec. II we make use of this periodicity to define certain subbands of the unperturbed electron and phonon energy bands, and we use these subbands to generate Green's func-

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[1] G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954).

[2] A. Seeger, J. Phys. Radium **23**, 616 (1962).

[3] J. Callaway, J. Math. Phys. **5**, 783 (1964).

[4] To avoid confusion we use the term *scattering resonance* rather than *virtual bound state*, so that *bound state* refers to a real localized state whose amplitude is significant only near the perturbed region.