circulation. As their contributions are much stronger than the contribution from the circulation in the weak central field of the vacancy, a negative spin-orbit splitting results. Thus the observed negative sign and magnitude of Δ indicate that the Z_1-center electron is vacancy centered and overlaps the surrounding lattice similar to the F-center electron. Moreover the insensitivity of Δ against $Ca^{++} \rightarrow Sr^{++}$ substitution suggests a non-nearest-neighbor site of the impurity ion at the vacancy. Similar conclusions have been drawn from the corresponding insensitivity of optical-absorption[6] and ENDOR[10] measurements. Thus the Faraday-rotation results lend strongest support to a vacancy-centered model of type C or D for the Z_1 center.

The absorption band at 2.4 eV accompanying the Z_1 band [Fig. 2(a)] resembles in relative location and spectral shape very much the K band of the F center. Following the interpretation by Smith and Spinolo,[17] its origin would be unresolved transitions into higher p states, which apparently for the Z_1 center have much higher relative oscillator strength than for the F center. Accurate experiments on the Faraday rotation of this band are under way.

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[1] H. Pick, Ann. Physik 35, 73 (1939).

[2] F. Seitz, Phys. Rev. 83, 134 (1951).

[3] H. Kawamura and K. Ishiwatari, J. Phys. Soc. Japan 13, 574 (1958).

[4] G. E. Conklin and R. J. Friauf, Phys. Rev. 132, 189 (1963).

[5] M. Ishiguro, E. Sugioka, and N. Takeuchi, J. Phys. Soc. Japan 15, 1302 (1960).

[6] H. Härtel and F. Lüty, Z. Physik 182, 111 (1964).

[7] P. A. Yurachkovskij and P. K. Gorbenko, Opt. i Spektroskopiya 20, 69 (1966) [translation: Opt. Spectry (USSR) 20, 35 (1966)].

[8] M. Kleefstra, J. Phys. Chem. Solids 24, 1687 (1963).

[9] G. Giuliani, Colloque sur les centres colorés, Saclay, France, March 1967 (unpublished).

[10] J. C. Bushnell, thesis, University of Illinois (unpublished).

[11] J. Mort, F. Lüty, and F. C. Brown, Phys. Rev. 137, A566 (1965).

[12] J. Margerie, Publ. Sci. Tech. Min. Air (France), Notes Tech. No. 155 (1966).

[13] C. H. Henry, S. E. Schnatterly, and C. P. Slichter, Phys. Rev. 137, A583 (1964).

[14] D. Y. Smith, private communication.

[15] F. C. Brown, B. C. Cavenett, and W. Hayes, Proc. Roy. Soc. (London) A300, 78 (1967).

[16] D. Y. Smith, Phys. Rev. 137, A574 (1965).

[17] D. Y. Smith and G. Spinolo, Phys. Rev. 140, A2121 (1965).

TRANSMISSION SPECTRA OF ZnO SINGLE CRYSTALS

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The fundamental absorption edge and the exciton structure of zinc oxide (ZnO) was first studied systematically by Thomas,[1] and the observation of exitons as polaritons has also been reported by Hopfield and Thomas.[2] The latter work was probably stimulated by results on the fundamental spectra of ZnO reported by Park et al.[3] Different interpretations for much of the experimentally observed structure have been given by these workers; a particular consequence of this is a discrepancy in the values quoted for both the spin-orbit interaction energy and the exciton binding energies. The difficulty derives from the interpretation of the reflection spectra which are highly complex near the absorption edge.

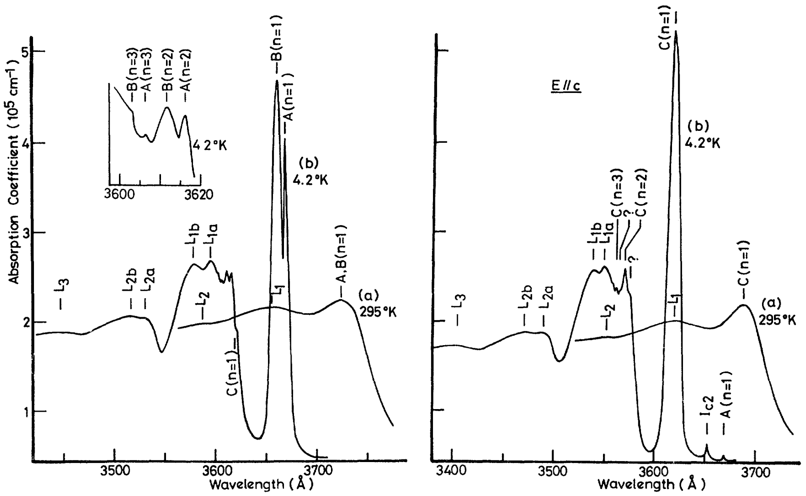
Transmission experiments using polarized light have been made on single crystals of ZnO at liquid-helium, liquid-nitrogen, and room temperatures. By using crystals as thin as 0.1 μm, transmission measurements have been made to photon energies greater than the band gap, and the method is similar to that used for wurtzite zinc selenide.[4] Thin platelets of ZnO were grown by the vapor transport method, using argon as the carrier gas. These crystals have the wurtzite structure with the c axis lying along the growth plane. Transmission electron-microscopy and -diffraction studies showed that most of these platelets were good single crystals free from defects such as stacking faults, though isolated crystals showed metal precipitates whose origin is not yet known.

The optical transmission study gave results for the exciton structure which are in good agreement with those obtained by Thomas[1] from reflection spectra. In addition, strong absorption peaks have been observed at energies greater than the band gap, even at 295°K. These new features cannot be explained in terms of interband or pure excitonic transitions. Figure 1(a) shows the absorption spectra of a 0.105-μm thick single crystal ZnO for $E \perp c$ at (a) 295°K and (b) 4.2°K; and Fig. 1(b) shows the spectra for $E \parallel c$. No correction for reflection loss has been made, and the absorption coefficient is therefore significant only for values greater than 10^5 cm^{-1}. It can be seen that, excluding bound exciton absorption peaks, which occur at energies smaller than or on the rising slope of the absorption edge, the main absorption peaks may be divided into two classes:

(i) Intrinsic exciton absorption.—These are labeled A, B, and C, with n indicating different quantum states. The intrinsic exciton peaks are extremely sensitive to changes in temperature and their intensity increases markedly on cooling. This is best illustrated by the appearance of their excited states at 4°K but not at 77°K (spectra at 77°K not shown). The positions of these transitions at 4.2°K, and their polarizations, are given in Table I.

The assignment of peaks $A(n=2)$ and $B(n=2)$ is based, at present, only on their strength and linewidth in comparison with their respective ground states [see Fig. 1(a) insert]. The second excited state ($n=3$) is in accord with the $1/n^2$ relation for the energies of successive quantum states, assuming Mott-Wannier–type excitons. This also results in very similar exciton binding energies for all the three valence bands, and these are $R_A = 0.0668 \pm 0.0005$ eV, $R_B = 0.0625$ eV, and $R_C = 0.0610 \pm 0.0005$ eV, respectively. A shoulder (3575 Å) appears on the low-energy side of $C(n=2)$. A weak transition was observed at 3565.6 Å which cannot be accounted for by the simple $1/n^2$ energy relation. The oscillator strength for the ground-state exciton is given qualitatively in Table I for the two modes of polarization. Although the oscillator strength of $A(n=1, E \perp c)$ was smaller than that of $B(n=1, E \perp c)$, their sum was similar to that of $C(n=1, E \parallel c)$ as predicted by Hopfield.[5] It is well known that the p-like valence band is split by the spin-orbit and crystal-field interactions. The valence-conduction band separations were calculated as the exciton series limit assuming a $1/n^2$ energy relation (Table I), which then give the valence-band separations $E_{BA} = -0.0032 \pm 0.0007$ eV, and $E_{BC} = +0.0393 \pm 0.0007$ eV. Applying the theory of the quasicubic model,[5] we obtain values for spin-orbit splitting $= -0.0047 \pm 0.0007$ eV and crystal-field splitting $= +0.0408 \pm 0.0007$ eV.

We have taken the zero for the energy at the



(1a)

(1b)

FIG. 1. (a) Absorption spectra of a thin wurtzite ZnO crystal at (A) 295°K, and (B) 4.2°K for light polarized $E \perp c$. (b) Absorption spectra of a thin wurtzite ZnO crystal at (A) 295°K, and (B) 4.2°K, for light polarized $E \parallel c$. I_{c2} is an impurity-bound exciton. For other transitions see text.

Table I. Position of the intrinsic excitons and the calculated band gaps in ZnO at 4.2°K.

Exciton		Polarization and Strength	Position (Å)	(ev)
A	$n = 1$	$E\perp c$ (strong)	3670.1	3.3781
		$E\parallel c$ (weak)	3670.5	3.3777
	$n = 2$	$E\perp c$	3616.5	3.4282
	$n = 3$	$E\perp c$	3606.6	3.4375
	$n = \infty$	(calculated gap)		3.4449
B	$n = 1$	$E\perp c$ (strong)	3661.9	3.3856
	$n = 2$	$E\perp c$	3612.0	3.4324
	$n = 3$	$E\perp c$	3602.8	3.4412
	$n = \infty$	(calculated gap)		3.4481
C	$n = 1$	$E\parallel c$ (strong)	3618.3	3.4264
		$E\perp c$ (weak)	3619	3.425
	$n = 2$	$E\parallel c$	3570.7	3.4722
	$n = 3$	$E\parallel c$	3561.9	3.4808
	$n = \infty$	(calculated gap)		3.4874

Energy of exciton phonon complexes at 4.2°K.

	$E\perp c$		$E\parallel c$	
	Energy (ev)	Separation from average exciton ground state (ev)	Energy (ev)	Separation from exciton ground state (ev)
L_{1a}	3.448	0.066	3.492	0.066
L_{1b}	3.464	0.082	3.505	0.079
L_{2a}	3.511	0.129	3.553	0.127
L_{2b}	3.525	0.143	3.573	0.147
L_3	3.599	0.217	3.643	0.217

band B in this calculation, and this results in a negative spin-orbit splitting energy. The choice is consistent with the polarization dependence of $A(n=1)$ and $B(n=1)$.[1] The negative value of the spin-orbit interaction energy is a direct consequence of the negative contribution from the zinc d band in the valence band.[6] The introduction of the d-wave function into the conduction and valence bands may also be responsible for giving a smaller minimum gap in ZnO than might be expected from the sequence in the zinc chalcogenides[7] (minimum gap in ZnTe 2.38 eV, in ZnSe 2.85 eV, and in ZnS 3.90 eV).

(ii) Exciton-phonon complexes (EPC).—Transitions due to what we term EPC are labeled (L_{1a}, L_{1b}), (L_{2a}, L_{2b}), etc. These transitions are observable at 295°K, and their intensity increases only moderately on cooling when compared with pure excitonic transitions. The different temperature dependence has enabled us to distinguish these two classes of transition from what seem to be complicated spectra. The doublet features $(L_{1a}, L_{1b}$, etc.) can be observed at 77°K (spectra not shown), and as many as four major peaks have been observed at 4.2°K. The energies of three EPC transitions are given in Table I, together with their separation from the exciton ground states. For $E\perp c$, an estimated average ground-state energy of 3.382 eV for excitons A and B has been used to calculate the separations.

It can be seen from Table I that the EPC peaks occur regularly at energy intervals which average 0.073 eV; this is close to the measured longitudinal optic (LO) phonon energy at $k=0$.[8,9] However, the observed peaks should not be thought of as simply due to phonon emission stimulated by the excitons in the crystals, but rather as transitions into complexes. The energy of these complexes will not in general be a simple sum of the exciton and phonon energies. In addition, more than one phonon may be involved in the formation of these complexes, as L_2 and L_3, etc. Preliminary results for other zinc chalcogenides show that the energy of the first EPC peak is a fraction smaller than the sum of the exciton ground state and LO phonon energies (separation ~ 0.9 of LO phonon energy). The EPC peak is much weaker and no doublet has been observed in these materials. The doublet structure in ZnO is probably a result of configuration interaction.

In general, EPC transitions are favored in solids of increasing ionic character, where the lattice can be readily polarized. The mechanism for the formation of the EPC remains to be explored. We believe that a weak EPC transition has been observed in GaAs,[10] and strong transitions in GaS, GaSe,[11] and MgO, though in the case of MgO the transition has been interpreted as the spin-orbit split-off peak.[12]

Direct measurements of the absorption spectra of ZnO have given an unambiguous interpretation of the exciton structure and valence-band splittings at the minimum gap, which we believe lies at the center of the Brillouin zone. In the case of intense exciton peaks as formed in ZnO, there can be some confusion in the spectra if the incident light is not completely polarized in the desired direction. It is possible that this occurs in the reflectivity measurement of Park et al.,[3] where a small percentage of residual polarization may be present due to off-normal incidence. Furthermore, they recorded the reflection spectra on photographic plates, and it would seem that the light from the source was incident on the crystal prior to entering the spectrograph. This could add a complication as both emission and reflection peaks can be recorded. Recognition of the exciton-phonon complexes may lead to the reinterpretation of a number of absorption spectra previously obtained.

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[1] D. G. Thomas, J. Phys. Chem. Solids 15, 86 (1960).

[2] J. J. Hopfield and D. G. Thomas, Phys. Rev. Letters 15, 22 (1965).

[3] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Bull. Am. Phys. Soc. 10, 331 (1965), and Phys. Rev. 143, 512 (1966).

[4] W. Y. Liang and A. D. Yoffe, Proc. Roy. Soc. (London) A300, 326 (1967).

[5] J. J. Hopfield, J. Phys. Chem. Solids 15, 97 (1960).

[6] K. Shindo, A. Morita, and H. Kamimura, J. Phys. Soc. Japan 20, 2054 (1965).

[7] The authors are grateful to Professor J. C. Phillips who suggested that as the covalent volume of the chalcogenide ions shrinks drastically in going from tellurium to oxygen, the role of the Zn *d* bands in the energy-band structure increases. In ZnO, the ratio of oxygen to zinc covalent volume is about 0.13, compared with the ratio of 0.50, 0.66, and 1.02 for ZnS, ZnSe, and ZnTe, respectively. The gross effect of increasing the proportion of the Zn *d*-wave function in the determination of the energy-band structure will lead to a reduction in the minimum gap at the center of the Brillouin zone. This argument is speculative and must be confirmed by detailed band-structure calculations.

[8] T. C. Damen, S. P. S. Porto, and B. Tell, Phys. Rev. 142, 2, 570 (1966).

[9] S. S. Mitra, J. Phys. Soc. Japan Suppl. 21, 61 (1966).

[10] M. D. Sturge, Phys. Rev. 127, 768 (1962), Fig. 3 (21°K).

[11] J. A. Wilson, unpublished.

[12] D. M. Roessler and W. C. Walker, Phys. Rev. 159, 733 (1967), Fig. 4.

THEORY OF ANTISYMMETRIC EXCHANGE IN RARE-EARTH SYSTEMS*

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The purpose of this Letter is to present a calculation of the Coulomb exchange interaction between an electron in a Kramers doublet and a second electron, demonstrating that the resultant exchange splitting contains both anisotropic symmetric and antisymmetric contributions of comparable magnitude and of exactly the same physical origin. That the antisymmetric exchange is of the same magnitude and of the same physical origin as the anisotropic exchange is of especial interest since simulating the Coulombic exchange interaction between electrons with the spin-permutation operator $\vec{S}_1\cdot\vec{S}_2$ fails to produce the antisymmetric contribution to exchange in a similar situation, though readily yielding the anisotropic part of symmetric exchange. The failure of the $\vec{S}_1\cdot\vec{S}_2$ interaction to produce antisymmetric exchange on the same level as anisotropic exchange is therefore due to a deficiency in the simulated exchange operator and does not imply a difference in physical origin of the two effects.

Antisymmetric exchange, or, as it is sometimes called, the Dzyaloshinsky-Moriya interaction between two spins, has the form $\vec{D}\cdot(\vec{S}_1\times\vec{S}_2)$. The interaction was first proposed by Dzyaloshinsky[1] from symmetry considerations to explain the weak ferromagnetism of α-Fe_2O_3. Moriya[2] subsequently developed a microscopic model to explain the origin of the antisymmetric exchange vector $\vec{D}$. His calculation was a perturbation calculation in the parameter λ/Δ, where λ is the spin-orbit coupling and Δ is a crystal-field splitting. In this calculation, antisymmetric exchange appears first in the second order of perturbation as a cross effect between off-diagonal exchange and spin-orbit coupling. Numerous recent experiments have shown that antisymmetric exchange en-