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Electroreflectance Measurements on Mg_2Si, Mg_2Ge, and Mg_2Sn[†]

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The room-temperature electroreflectance spectra of the II–VI compounds Mg_2Si, Mg_2Ge, and Mg_2Sn are reported in the energy region 1.5–4.5 eV. All measurements were performed using the electrolyte technique with a nonaqueous electrolyte. These materials crystallize with the antifluorite crystal structure and are small-band-gap semiconductors. In all of the materials, a large number of sharp peaks were observed; the spectra are interpreted in terms of the reflectivity spectra and existing energy-band calculations. Special mention should be made of a doublet observed (1.64–1.84 eV) in the spectrum of Mg_2Ge. This doublet appears to be due to the spin-orbit splitting of the Γ_{15} valence band.

INTRODUCTION

THE examination of the reflectivity spectra of a family of materials with the same crystal structure and constituent atoms which vary within a given column of the periodic table has been a powerful technique for studying energy bands.[1] This technique has been most extensively applied to the zincblende-germanium family (fcc), although other families have also been investigated (e.g., lead chalcogenides, wurtzite, monovalent metals). Since the outer electronic configurations of the atoms in a given family are the same, one expects close similarities in their energy bands, and hence in their optical properties. Such similarities are confirmed by experiment. From the large variation of the spin-orbit interaction as one proceeds down a particular column of the periodic table, and from the knowledge of the atomic spin-orbit splittings, assignments of certain critical points in the optical spectra are made. Assignments based on spin-orbit splittings are usually the most reliable. Any other assignments are subject to final confirmation through calculations of optical constants from a reliable band structure.

The resolution of reflectivity measurements is greatly enhanced by the use of modulation techniques, among which electroreflectance[2] occupies a rather prominent place because of its simplicity. We have used this approach to study the family Mg_2X (X=Si, Ge, Sn). The study of these materials is a logical extension of the study of the zincblende-germanium family. Their crystal structure (antifluorite) is also fcc and the number of valence electrons per unit cell is the same as for zincblende. These materials are small-band-gap semiconductors[3–5]; hence most of the interesting optical transitions are found in or near the visible region of the spectrum. Further, all of the constituent atoms (with the possible exception of Pb, which may require relativistic corrections) should be easy to handle in a conventional band-structure calculation.[6,7] Experience with and programs for other fcc materials can be easily adapted to Mg_2X. In particular, the pseudopotential form factors of the group-IV atoms, which are rather precisely known, could reduce adjustable parameters in semiempirical calculations.

Our electroreflectance measurements were performed at near normal incidence at room temperature using the electrolyte technique[2] on samples of Mg_2Si, Mg_2Ge, and Mg_2Sn over the energy region 1.5–4.5 eV. In a few cases, spin-orbit splittings are apparent in the electroreflectance spectra and have been used to assign critical points in the band structure. Previous theoretical calculations of the band structures of these materials had been attempted[6,7] in the absence of extensive experimental data on the optical properties. We have made tentative assignments of the observed structure on the bases of these calculations, keeping in mind their qualitative nature.

EXPERIMENTAL METHOD

All of the electroreflectance measurements were made using the electrolyte technique.[2] Because of the reactivity of the Mg_2X materials to water, the nonpolar electrolyte produced by a saturated solution of dried tetrabutyl ammonium perchlorate in propylene carbonate was used. As long as this solution was not allowed to pick up water vapor from the atmosphere, the cleaved crystal surfaces appeared unaffected by at least several days immersion in the electrolyte.

Since all of the Mg_2X materials cleave easily, all measurements were made on cleaved surfaces. The cleavage face in all cases was a (111) plane, and looked like a slightly blue mirror. Electrical contacts were

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[1] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. 18, p. 1.

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[3] G. Busch and U. Winkler, Physica **20**, 1067 (1954).

[4] U. Winkler, Helv. Phys. Acta **28**, 633 (1955).

[5] Mg_2Pb, another material of this family which we have not measured, has been reported to be metallic. See Ref. 3.

[6] P. M. Lee, Phys. Rev. **135**, A1110 (1964).

[7] N. O. Folland, Phys. Rev. **158**, 764 (1967).

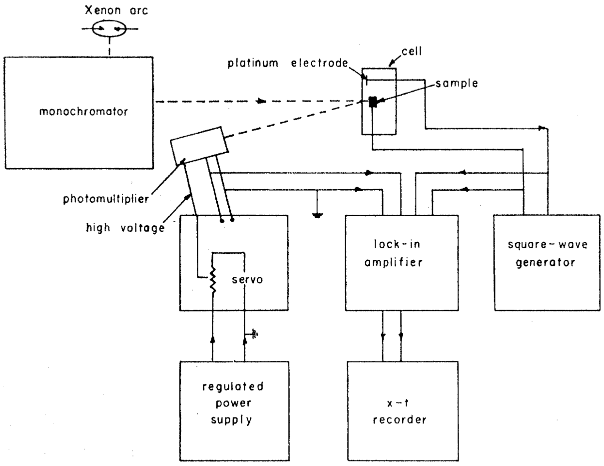

FIG. 1. Experimental setup used for electroreflectance measurements by the electrolyte technique.

made to the backs of the samples with silver paint, and insulating varnish was applied over the contact and the wire to isolate them from the electrolyte.

Crystals were cleaved and contacts were made while the sample was inside a glove bag, continuously flushed with dry nitrogen gas to prevent deterioration of the surfaces from contact with water vapor; these precautions were most necessary with Mg_2Ge and Mg_2Si because of their high reactivity with water. The prepared samples were then introduced into the electrolyte before removal from the glove bag to the spectrometer.

The experimental setup was the standard one used for electrolyte electroreflectance, and is shown in Fig. 1. A zero-based square-wave generator operating at 100 Hz was used as the modulation voltage; the high resistance of the electrolyte restricted the maximum frequency of operation, and 100 Hz was a compromise between low-frequency noise and signals which grew weaker with increasing frequency. No bias voltage was used, and the typical ac voltages used were less than 2V (higher-voltage modulation often produces chemical reaction of the samples, which is more pronounced if any water is present in the electrolyte). A Spex model 1700-II $\frac{3}{4}$-m Czerny-Turner grating monochromator was used with either a 600-line/mm grating blazed at 500 mμ or a 1200-line/mm grating blazed at 200 mμ. A 450W Osram Xenon arc, quartz optics, and either a Dumont 6911 phototube or an EMI 6252B phototube, depending on spectral region, completed the optical system. All experiments were performed at room temperature.

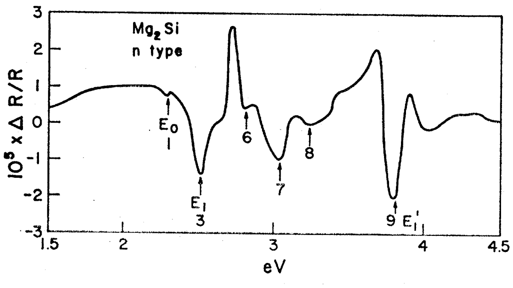

FIG. 2. ER spectrum of n-type Mg_2Si at room temperature.

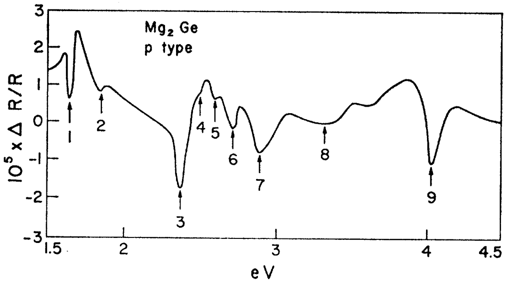

FIG. 3. ER spectrum of p-type Mg_2Ge at room temperature.

The samples of Mg_2Si and Mg_2Sn were n type and those of Mg_2Ge were p type. No attempts were made to change carrier type or concentration in any of the samples.

RESULTS AND DISCUSSION

The electroreflectance spectra of all three materials are presented in Figs. 2–4, and the transition energies derived from these spectra are listed in Table I in the columns labeled ER. For comparison we also show in Fig. 5 and Table I the unpublished results of Scouler[8] on the reflectivity (R) of these materials at 77°K and the positions of structure in ϵ_2 as determined from his curves of ϵ_2 obtained from the Kramers-Kronig analysis of the reflectivity. The similarity among the electroreflectance and the reflectivity peaks is easily seen, as is the systematics of the dependence on the different group-IV elements. In Table I we have numbered the peaks for ease of discussion. The correlation implied by the numbering of the peaks in the three materials measured was arrived at by considering the line-shape similarities in both the reflectivity and the electroreflectance spectra. In some cases (see, for instance, peak 9 of Fig. 4), it is subject to some arbitrariness.

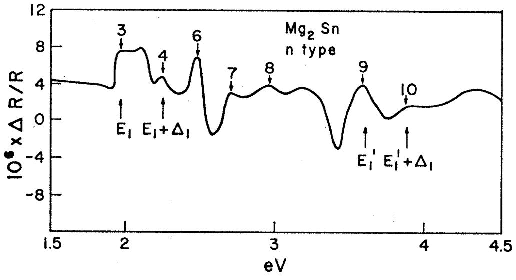

FIG. 4. ER spectrum of n-type Mg_2Sn at room temperature. Notice that the sign of the peaks is opposite to that in Figs. 2 and 3. Such sign is not determined by the carrier sign but by the sign of the band bending at the surface.

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[8] W. J. Scouler, Phys. Rev. (to be published).

TABLE I. Peaks observed in the reflectivity (R) and the electroreflectance (ER) spectra of Mg_2Si, Mg_2Ge, and Mg_2Sn. Also, peaks in ϵ_2 calculated from the reflectivity data (Ref. 8).

		Mg_2Si			Mg_2Ge			Mg_2Sn		
Peak	Proposed transition	R	ϵ_2	ER	R	ϵ_2	ER	R	ϵ_2	ER
1	$E_0(\Gamma_{15}$-$\Gamma_1)$	2.17	2.18	2.27	1.67	1.7	1.64	...	...	...
2	$E_0+\Delta_0$	...	...	...	...	...	1.84	...	...	...
3	$E_1(\Lambda_3$-$\Lambda_1)$	2.75	2.70	2.51	2.57	2.57	2.37	2.12	2.12	1.96
		...	...	2.61	...	...	...	...	...	2.11
4	$E_1+\Delta_1$	...	...	...	...	...	2.50	2.30	2.26	2.24
5		...	...	...	...	...	2.60	...	...	...
6		2.85	...	2.78	...	...	2.71	2.50	2.45	2.48
7		...	...	3.05	3.00	2.90	2.88	2.73	2.63	2.70
8		3.33	...	3.28	3.47	...	3.31	2.96	...	2.96
9	E_1'	3.83	3.80	3.80	4.00	4.07	4.03	3.41	3.50	3.60
10	$E_1'+\Delta_1$							3.83	...	3.89

The peaks are also subject to the usual arbitrariness in the definition of the peak energy in the absence of a quantitative understanding of the line shape. In all of these Mg_2X ($X=$Si, Ge, Sn) materials, the fundamental optical gap has been found to be of the indirect type. This gap in Mg_2Si has been reported to be in the range 0.66–0.78 eV by various investigators.[4,9,10] The shape of the absorption edge[11] suggests that the transition is indirect.[10] From electrical and optical measurements, the fundamental gap in Mg_2Ge has been found to lie in the range 0.57–0.74 eV,[3,10,12–15] again being a transition of the indirect type.[15,16] In Mg_2Sn the gap has been reported in the range 0.16–0.33 eV on the basis of electrical,[6] optical,[17,18] and photoconductivity measurements[16–18]; electrical measurements indicate that its conduction-band minima lie along the [100] directions.[19] In the case of Mg_2Ge, infrared measurements of free-carrier absorption in *p*-type material[15] yielded a value for a spin-orbit splitting of the top valence band of 0.20 eV; on the basis of this value, splittings of 0.03eV for Mg_2Si and 0.60 eV for Mg_2Sn have been predicted.[15] All existing band-structure calculations[6,7] unanimously assigned this top of the valence band to the Γ_{15} state at $\mathbf{k}=0$.

In view of the discussion above, we assign peaks 1 and 2 in Fig. 3 to transitions[20] across the lowest direct gap at $\mathbf{k}=0$ ($\Gamma_{15}\rightarrow\Gamma_1$): the 1-2 splitting (0.2 eV), in agreement with the measurements of Lott and Lynch,[15] represents the spin-orbit splitting of the Γ_{15} state. Such splitting is reasonable in view of the fact that the corresponding splitting for crystalline germanium is 0.3 eV; it suggests that the electron at Γ_{15} spends $\frac{2}{3}$ of its time around the Ge and $\frac{1}{3}$ around the Mg atoms.[21] The ratio of the intensities of peaks 1 and 2 is in agreement with the interpretation based on spin-orbit splitting. Peak 1 is present in both the ER and R spectra of Mg_2Si; peak 2 is unresolved, as expected (Δ_0 being too small). Since we have not observed such peaks for Mg_2Sn, we assume they occur in the infrared, beyond the range of our measurements. Measurements in this region are in progress and will be reported later.

The energy of peak 1 of Mg_2Si agrees well with the value calculated by Folland[7] for the Γ_{15}-Γ_1 gap (2.1 eV). For Mg_2Ge our experimental energy (at room temperature) is somewhat smaller than the value of 1.74 eV at 195°K reported by Mead; the temperature coefficient of the Γ_{15}-Γ_1 gap[4] would, at least, reduce the

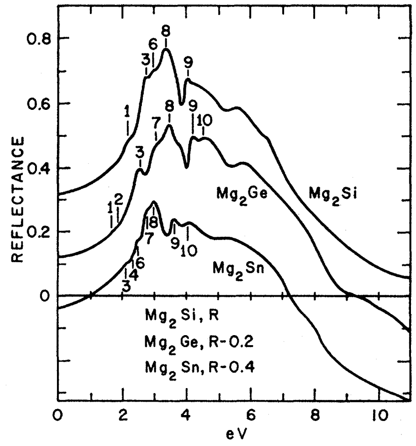

FIG. 5. Reflectance spectra of Mg_2Si, Mg_2Ge, and Mg_2Sn according to Scouler (Ref. 8). For display purposes the vertical scales have been shifted as indicated.

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[19] J. Umeda, J. Phys. Soc. Japan **18**, 2052 (1964).

[20] The corresponding transitions are usually labeled E_0 and $E_0+\Delta_0$ in the germanium-zincblende family.

[21] This fraction of time spent around each component was used in Ref. 15 to calculate Δ_0 for Mg_2Si and Mg_2Sn. We have repeated the calculation with the known Δ_0 for α-Sn (Ref. 2), and obtained $\Delta_0=0.48$ instead of 0.60 eV.

discrepancy to something in the neighborhood of the experimental error. The peaks numbered 3 on the three compounds are considered as a possible E_1 transition ($\Lambda_3 \rightarrow \Lambda_1$ or $L_{3'} \rightarrow L_1$ in the usual zincblende notation). They appear as leading peaks in the reflectivity spectra as it happens in group IV and group II-VI compounds. The similarity of the reflectance spectra of the diamond and zincblende structures has been extensively discussed in the literature. We are taking the suggestions of Lee[6] and Della Ricia[22] that the dominant features of the reflectance spectra should be determined by the shape of the Brillouin zone; this makes a comparison between the diamond and zincblende compounds and the present compounds a reasonable first step in interpreting these spectra.

Peaks numbered 4 are tentatively assigned to $E_1+\Delta_1$ transitions, i.e., the spin-orbit split component of the E_1 peak. This splitting Δ_1 corresponds to 0.13 eV for Mg_2Ge and thus agrees well with $\frac{2}{3}$ of Δ_0. The splitting Δ_1 equals 0.28 eV for Mg_2Sn, in agreement with the value predicted by the $\frac{2}{3}$ rule from the $\Delta_0=0.48$-eV splitting mentioned above.[21] Otherwise, this peak on the three compounds corresponds to peaks in ϵ_2 that agree with the character M_1 of Lee's[2] calculation.

With more uncertainty, we have attributed the structure numbered 9 to an E_1' transition because it appears in the same relative position in the reflectance spectrum as in the diamond and zincblende compounds. Peak 10, observed only in Mg_2Sn, could be the spin-orbit splitting 9, since it gives about the same value of 0.29 eV for Δ_1 as peaks 3 and 4. It appears as an M_2 transition in Lee's calculation and as a peak in ϵ_2 in Scouler's[16] results.

We shall refrain at this point from any more tentative assignments of the remaining structure shown in Figs. 2–4. This structure should easily be interpretable as soon as the next generation of band-structure calculations becomes available.

Note added in proof. A recent pseudopotential band-structure calculation by M. Y. Au-Yang and M. L. Cohen to be published in this journal supports the above assignments and further interprets the spectra. Unpublished OPW calculations by F. Herman also support our general conclusions.

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[22] J. Della Ricia, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 51.

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Magnon Corrections to the Effective Mass of an Electron in a Magnetic Semiconductor*

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We have computed the renormalization of the conduction-electron energy in a degenerate ferromagnetic semiconductor at zero temperature due to the virtual emission and reabsorption of spin waves. We find that as a result of the difference between the up- and down-spin Fermi momenta, this renormalization is quite small. However, in the case where the conduction electrons are antiferromagnetically coupled to the ionic moments, it is possible by doping to achieve a situation in which the effective mass of the down-spin electrons is increased by about 30%, while the up-spin electrons remain unaffected.

I. INTRODUCTION

MAGNETIC semiconductors have received a great deal of attention recently.[1] One reason for this is the possibility of extending the technological applications of semiconductors. Another reason is the hope that by doping these materials, one might gain some insight into the nature of band magnetism.

In the presence of such doping, one might ask how the conduction electrons affect the magnetic properties, or, alternatively, how the magnetic order affects the transport properties. The first type of question involves, for example, the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[2] The second type of question has

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† National Science Foundation Predoctoral Fellow.

[1] Symposium on Magnetic Semiconductors (invited talks), Bull. Am. Phys. Soc. **13**, 368 (1968).

[2] See, e.g., F. Holtzberg, T. McGuire, S. Methfessel, and J. Suits, Phys. Rev. Letters **13**, 18 (1964).