*Present address: Naval Research Laboratory, Washington, D. C.

[1]D. Shoenberg, Phil. Trans. Roy. Soc. (London) A255, 85 (1962).

[2]A. B. Pippard, Proc. Roy. Soc. (London) A272, 192 (1963).

[3]J. R. Anderson and A. V. Gold, Phys. Rev. Letters 10, 227 (1963).

[4]C. Kittel, Phys. Rev. Letters 10, 339 (1963).

[5]R. D. Plummer and W. L. Gordon, Phys. Rev. Letters 13, 432 (1964).

[6]M. H. Halloran and F. S. L. Hsu, Bull. Am. Phys. Soc. 10, 350 (1965). See also J. LePage, M. Garber, and F. J. Blatt, Phys. Letters 11, 102 (1964); J. LePage, M. Garber, and F. J. Blatt, in Proceedings of the Ninth International Conference on Low-Temperature Physics (Plenum Press, New York, 1965), p. 799.

[7]J. E. Kunzler, F. S. L. Hsu, and W. S. Boyle, Phys. Rev. 128, 1084 (1962).

[8]B. D. McCombe and G. Seidel, in Proceedings of the Ninth International Conference on Low-Temperature Physics (Plenum Press, New York, 1965), p. 794.

[9]The beryllium used in these measurements was kindly loaned to us by Nuclear Metals, Inc., Concord, Massachusetts. The state resistivity ratio was 3300.

[10]B. R. Watts, Phys. Letters 3, 284 (1963).

[11]T. L. Loucks and P. L. Cutler, Phys. Rev. 133, A819 (1964); T. L. Loucks, Phys. Rev. 134, A1618 (1964).

OBSERVATION OF PHONON ASSISTED INDIRECT TRANSITIONS BY STRESS MODULATED OPTICAL TRANSMISSION

W. E. Engeler, M. Garfinkel, and J. J. Tiemann

General Electric Research and Development Center, Schenectady, New York

(Received 10 January 1966)

Recently, the periodic stress modulation of the reflectivity of semiconductors[1,2] and metals[1,3,4] has been shown to provide useful information about the band structure of solids. In principle, if these data are taken over a sufficiently wide energy range, they will yield, after a Kramers-Kronig analysis,[3,4] all of the information that may be obtained concerning the changes in optical constants due to strain. In practice, however, this reflectivity technique is sufficiently sensitive to detect only the changes in the strong direct optical transitions. The relatively weak phonon-assisted transitions at the indirect edge of Ge, for example, are not observed.[1] This Letter reports the results of an experiment where the stress modulation of the optical properties is measured by means of the transmitted beam. The results at room temperature clearly show the phonon and exciton structure associated with the indirect edge of Ge. The allowed transitions are clearly distinguished from the forbidden ones, and the indirect band gap, the dilatation and pure shear deformation potentials, and the phonon energies at L can all be directly observed.[5] This experimental method should be generally useful for studying the band structure and phonon dispersion curves of less well-known indirect semiconductors.

Figure 1 shows a schematic diagram of the apparatus used for the experiment. A polarized monochromatic beam, modulated at f_1, is sent through the sample onto a detector. The sample, which is the central leg of a three-post yoke, undergoes a periodic strain at the frequency f_2. The sample is driven by two matched lead-zirconate-titanate-type transducers which comprise the other two legs of the yoke. The signal received at the detector is analyzed for both frequencies f_2 and f_1 by means of two phase-sensitive lock-in amplifiers. A voltage proportional to the amplitude of the signal at f_1, $A(f_1)$, is fed back to a servo controlling the monochromator which maintains a constant transmitted intensity. To first order the ratio of the am-

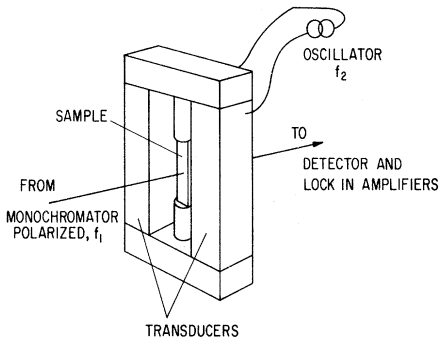

FIG. 1. Schematic view of experimental apparatus.

plitude of the signals at f_2 and f_1 yields

$$A(f_2)/A(f_1)=\sqrt{2}\,t\Delta\alpha, \qquad (1)$$

where t is the thickness of the sample and $\Delta\alpha$ is the change of the absorption constant with strain.[6] Figure 2 shows this ratio plotted against wavelength for two samples of Ge subjected to uniaxial stress along the ⟨100⟩ direction (sample 1) and the ⟨110⟩ direction (sample 2), with the light polarized parallel and perpendicular to the stress axis.

The results can best be described in terms of the changes in the dielectric constant $\Delta\epsilon_1 + i\Delta\epsilon_2$. Since the dielectric constant $\epsilon_1 + i\epsilon_2$ and the strain e are both symmetric second-rank tensors, six independent components are needed in $m3m$ symmetry to specify completely the effect of a general strain on the optical properties of Ge.[2,7] The general relation

$$(\Delta\epsilon_1 + i\Delta\epsilon_2)_{pj} = (w_1 + iw_2)_{pjkl}\, e_{kl} \qquad (2)$$

can therefore be written in the usual reduced notation,[8] with the six independent components $(w_1)_{11}$, $(w_2)_{11}$, $(w_1)_{12}$, $(w_2)_{12}$, $(w_1)_{44}$, and $(w_2)_{44}$. By a suitable combination of experiments, such as those shown in Fig. 2, the changes in the imaginary part of the dielectric constant $\Delta\epsilon_2$ and therefore the three imaginary components of the piezo-optical interaction tensor W may be determined.

Corrections must be made for the changes in the thickness of the sample and the strain induced changes of the reflectivity. The latter correction requires a knowledge of $\Delta\epsilon_1$. This was measured in an independent experiment utilizing an interferometric technique.[9] The results of this measurement at 0.722 eV are: $(w_1)_{11}=54$, $(w_1)_{12}=63$, and $(w_1)_{44}=38$. These values were used in the calculation, and were assumed to be independent of wavelength over the range of the experiment. These results are in disagreement with previous measurements of the change of index of refraction with hydrostatic pressure.[10]

The results for $(w_2)_{11}$, $(w_2)_{12}$, and $(w_2)_{44}$ are shown in Fig. 3. The values of $(w_2)_{11}$ and $(w_2)_{12}$ were obtained from sample 1 and $(w_2)_{44}$ was obtained from sample 2.

The interpretation of these curves is complicated somewhat by the fact that each sample, in addition to the ac stress, is also subjected to a large static uniaxial tension. With the help

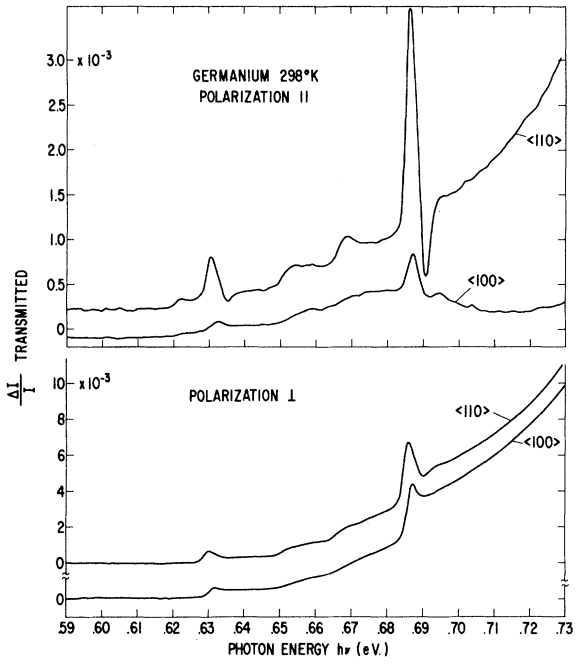

FIG. 2. Stress-induced changes in the transmission of Ge at 298°K. Sample 1 is stressed along a ⟨100⟩ direction and sample 2 is stressed along ⟨110⟩. Both samples presented a ⟨001⟩ face to the beam and were 0.53 mm thick. The light polarization directions are parallel and perpendicular to the stress axis.

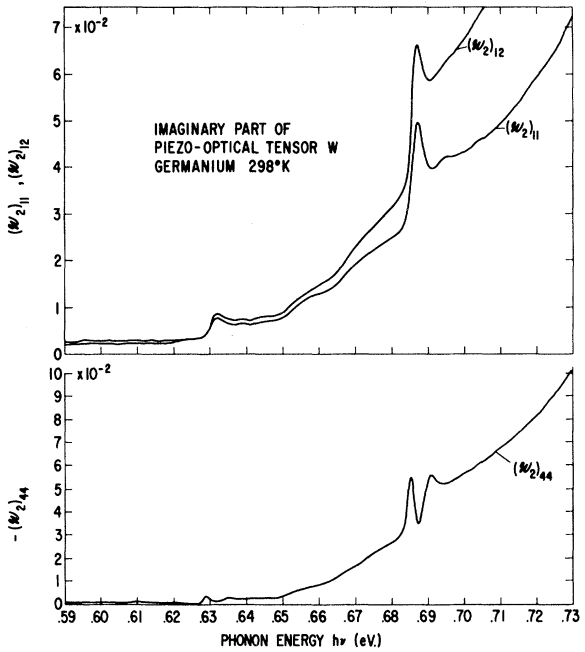

FIG. 3. Spectral dependence of the imaginary parts of the complex strain-optical tensor W.

of the deformation-potential model, the effects of the static stress can be determined, and most of the gross features of the data can be understood.

The deformation potential expression for the energy shifts of each of the valleys in Ge is,[11] neglecting the valence band splittings,

$$\Delta E_g^{(i)} = \vec{n}^{(i)} \cdot \{E_1(\mathrm{Tr}e)\mathbf{1} + E_2[e - \tfrac{1}{3}(\mathrm{Tr}e)\mathbf{1}]\} \cdot \vec{n}^{(i)}, \quad (3)$$

where $\vec{n}^{(i)}$ is a unit vector in the direction of the ith valley, $\mathbf{1}$ is the unit tensor, and[12] $E_1 = 4$ eV and[11,13] $E_2 = 16$ eV are the deformation potentials for the indirect band gap. This implies that a tension T along 100 causes no splitting of the valleys and that

$$\Delta E_g^{(i)} = \Delta E = -(s_{11} + 2s_{12})E_1 T_{100}. \quad (4)$$

The static uniaxial tension appled to sample 2, however, in addition to an average shift of

$$\langle \Delta E_g \rangle = -(s_{11} + 2s_{12})E_1 T_{110}, \quad (5)$$

causes a splitting of the (111) valleys. Two valleys move to higher energy and two valleys move more strongly to lower energy. The separation of these pairs of valleys is given by

$$\Delta E_g^{(u)} - \Delta E_g^{(l)} = \tfrac{1}{3} s_{44} E_2 T_{110}. \quad (6)$$

As will be shown, allowed transitions which involve valleys that shift to lower energy produce positive peaks in $\Delta\epsilon_2$, whereas minima result if the valleys are raised in energy. Thus, an allowed transition is sample 2 should appear as a strong peak together with a somewhat weaker dip which is higher in energy by the amount given by Eq. (6). This type of structure is clearly observed in the data. Using the observed splitting of 4.5 mV and the deformative potential previously quoted, a static strain of 4.1 $\times 10^{-4}$ is deduced. This value of strain should have caused a shift in the average energy of 1 mV. When a further correction for ambient temperature is applied, the observed energies agree with previous determinations to better than 0.5 mV which is the limit of experimental uncertainty. If the band-gap energy is known, the ratio of E_1 to E_2 can be unambiguously determined by this experiment. Further, if the static strain is measured, both E_1 and E_2 may be determined.

The structure exhibited by the data for sample 1 is most easily understood. For this sample, the uniaxial tension causes an equal lowering of the energy of all four valleys, and the ac component of the stress merely modulates this energy. If the transitions are to the lowest level of the indirect exciton, the additional absorption for an allowed transition has the form

$$(\epsilon_2)_{\mathrm{allowed}} = C(E - E_t)^{1/2}, \quad (7a)$$

and for forbidden transitions

$$(\epsilon_2)_{\mathrm{forbidden}} = C(E - E_t)^{3/2}, \quad (7b)$$

where $E_t = E_g - E_{\mathrm{ex}} \pm E_{\mathrm{phonon}}$ is the threshold energy for the transition.[14] As E_t undergoes a modulation by the applied ac stress, the changes in ϵ_2 are therefore

$$(\Delta\epsilon_2)_{\mathrm{allowed}} = \tfrac{1}{2} C(E - E_t)^{-1/2}(dE_t/de)e, \quad (8a)$$

$$(\Delta\epsilon_2)_{\mathrm{forbidden}} = \tfrac{3}{2} C(E - E_t)^{1/2}(dE_t/de)e, \quad (8b)$$

where e is the dilation.

From Eqs. (8a) and (8b), one can see that allowed transitions give rise to peaks in $\Delta\epsilon_2$ while forbidden transitions give rise to thresholds with no local maxima.

The shapes of the structure observed for sample 1 agree with the expected shapes. Transitions involving the LA and TO phonons appear as peaks while those involving the TA phonon produce thresholds. The identification of LA as allowed and TA as forbidden agrees with previous observations, and the identification of TO as allowed confirms the expectation based on group theory.[15]

The data from sample 2 can also be used to advantage to corroborate these observations. These data have the advantage that each peak is larger and is followed on the high-energy side by a dip, and each threshold is followed by a negative threshold of smaller size. Thus, the peaks all appear sharper, and the thresholds appear as steps. It can be shown that the quantity $(\Delta\epsilon_2)_{\parallel} + (\Delta\epsilon_2)_{\perp}$ does not involve $(w_2)_{44}$ and that except for the different static stress in samples 1 and 2, this particular combination should be the same for either sample. This combination is plotted in Fig. 4. The ratio of emission probability to absorption probability is given by

$$P_e/P_a = (N+1)/N = \exp(E_p/kT), \quad (9)$$

which has the values 2.92 and 1.35 for the LA

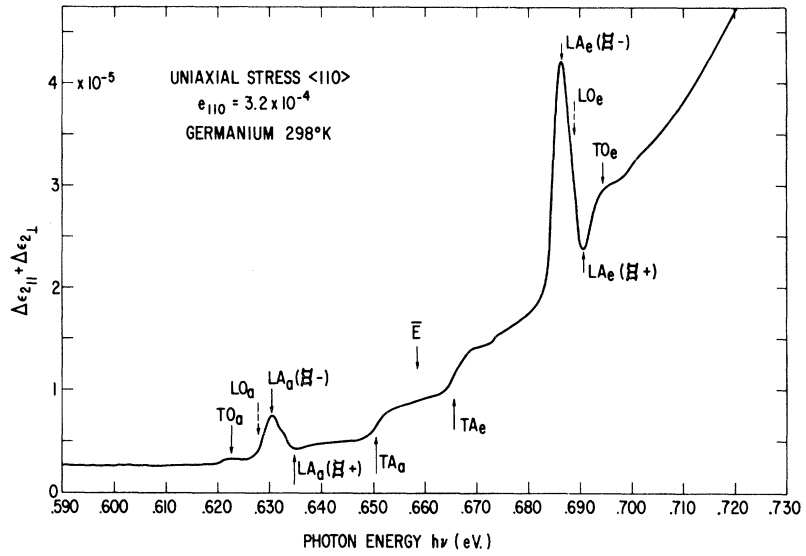

FIG. 4. Phonon assignments for sample 2. The same combination, $\Delta\epsilon_{2\parallel} + \Delta\epsilon_{2\perp}$, was made for sample 1 and was the source of the sample 1 energies by Table I.

and TA phonons, respectively. The observed ratios for either sample are 4.7 ± 0.2 and 1.6 ± 0.1, respectively.

The disagreement for the TA case is not too serious, although it is outside experimental error. The measured value for the LA case, however, departs significantly from Eq. (9). A possible explanation for this discrepancy is that the phonon energies are themselves strain dependent. Since this quantity appears in E_1 [see Eq. (7)] with opposite sign for emission and absorption, its stress dependence produces an effect of the type noted. If this were the correct explanation, the deformation potential for the phonon energy would be, for LA, $E_1 \approx -0.9 \pm 0.2$ V, and for TA, $E_1 \approx -0.4 \pm 0.2$ V. This is unreasonably large in view of previous determinations at lower temperature.[16] (This feature of the data is not understood at present.)

The phonon energies may be obtained by taking half the difference between the threshold energies for emission and absorption of each phonon. These energies together with the phonon energies previously measured by optical and tunneling experiments are tabulated in Table I.

In addition, the average of energies of the transitions, $\bar{E}$, corresponding to emission and absorption of each phonon is tabulated. This energy represents the energy difference between the top of the valence band and the lowest exciton state of each sample. When corrected for static strain by means of Eqs. (4), (5), and (6), a mean value of 0.6616 V is obtained. When corrected for temperature, this measurement agrees with that previously reported[10] to within 0.5 mV, as was previously mentioned.

Table I. Phonon energies of germanium at L.

	Phonon energy mV						
	Piezotransmission (room temperature)		Tunneling[a]	Tunneling[b]	Optical[c]	$\bar{E}$	
Phonon	⟨100⟩	⟨110⟩	(room temperature)	(1.8°K)	(291°K)	⟨100⟩	⟨110⟩
TA	7.6	7.7	7.6	7.805 ± 0.006	7.6	0.6603	0.6582
LA	27.7	$28.1(\Xi_-)$	27.5	27.49 ± 0.01	27.3	0.6594	$0.6584(\Xi_-)$
		$28.8(\Xi_+)$					$0.6626(\Xi_+)$
LO			31.6	30.55 ± 0.02	30.7		
TO	35.4	35.9	36.0	36.04 ± 0.01	36.7	0.6597	0.6584

[a]See Ref. 17. [b]See Ref. 16. [c]See Ref. 14.

Using a value of 2.7×10^{-3} V for the binding energy of the exciton, an indirect energy gap at 25°C of 0.6643 ± 0.0005 V is obtained.

In addition to these single-phonon transitions, there are also some indications of two-phonon processes at higher energies, as are observed in tunneling experiments,[17] but these are close to the noise level of the experiment. Because of the strong peak associated with the LA phonon transitions, the weak LO phonon is not observed. Its expected location is shown by a dotted arrow. The high-energy sides of the LA associated transition show additional unresolved structure which is probably due to transitions to the higher exciton states.

We are indebted to D. J. Locke for the fabrication of the samples used.

[1]W. E. Engeler, H. Fritzsche, M. Garfinkel, and J. J. Tiemann, Phys. Rev. Letters 14, 1069 (1965).

[2]G. W. Gobeli and E. O. Kane, Phys. Rev. Letters 15, 142 (1965).

[3]W. E. Engeler, M. Garfinkel, J. J. Tiemann, and H. Fritzsche, in Proceedings of the International Colloquium on Optical Properties and Electronic Structure of Metals and Alloys, Paris, 1965 (unpublished).

[4]W. E. Engeler, M. Garfinkel, and J. J. Tiemann, Bull. Am. Phys. Soc. 10, 1085 (1965).

[5]Phonon structure at the indirect edge of Ge has been observed at room temperature by means of the Franz-Keldysh effect: A. Frova and P. Handler Phys. Rev. 137, A1857 (1965). The structure observed in that experiment is very complex, however, and it has not been analyzed in detail.

[6]ac quantities are quoted as rms values throughout.

[7]J. F. Nye, Physical Properties of Crystals (Oxford University Press, London, 1957), p. 249 ff.

[8]J. F. Nye, Physical Properties of Crystals (Oxford University Press, London, 1957), p. 131 ff and 253.

[9]M. Garfinkel and W. Engeler, to be published.

[10]M. Cardona, H. Brooks, and W. Paul, J. Phys. Chem. Solids 8, 204 (1959).

[11]H. Brooks, in Advances in Electronics and Electron Physics, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 85.

[12]W. Paul, J. Phys. Chem. Solids 8, 196 (1959).

[13]C. Herring and E. Vogt, Phys. Rev. 101, 944 (1956).

[14]T. P. McLean, in Progress in Semiconductors, edited by A. F. Gibson (Heywood and Company, Ltd., London, 1960), Vol. 5, p. 53.

[15]T. P. McLean, in Progress in Semiconductors, edited by A. F. Gibson (Heywood and Company, Ltd., London, 1960), p. 84 (note added in proof).

[16]R. T. Payne, Phys. Rev. Letters 13, 53 (1964).

[17]A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. 125, 877 (1962).

SUPERCONDUCTIVITY IN FERROMAGNETIC ALLOYS

K. H. Bennemann and S. Nakajima*

Cavendish Laboratory, University of Cambridge, Cambridge, England

(Received 31 August 1965)

In a ferromagnetic alloy, the spins of the magnetic impurities are correlated and not free to rotate. Then the exchange interaction between conduction electrons and magnetic impurities involves energy transfer. Therefore the theory proposed by Gor'kov and Rusinov[1] on superconductivity in ferromagnetic alloys assuming a static exchange interaction is extended by using a time-dependent exchange interaction between conduction electrons and magnetic impurities.[2] The system of impurity spins is treated by quantum field-theoretical methods using the special technique developed by Abrikosov.[3] The electron-electron interaction resulting from the exchange of magnons is included in the effective electron-electron interaction. The electronic self-energy resulting from the dynamic electron–spin-wave coupling is determined analogously as in the case of dynamic electron-phonon coupling by Éliashberg.[4] The dimensionless electron–magnetic-impurity exchange coupling constant turns out to be much bigger than the dimensionless electron-phonon coupling constant.

There is no indication so far that the anomalous electronic scattering derived by Kondo[5] for exchange coupling between conduction electrons and magnetic impurities is significant for superconducting paramagnetic alloys. This anomalous electronic scattering decreases with decreasing degeneracy of the impurity-spin energy levels and increasing Zeeman energy of the impurity spins and thus should become even less important for superconducting ferromagnetic alloys. Therefore it should be possible in any case to isolate effects arising from Kondo's anomalous electronic scattering from the effects arising from electron–spin-