[1] C. Chr. Schüler, Phys. Letters 12, 84 (1964).

[2] H. Miwa, Progr. Theoret. Phys. (Kyoto) 29, 477 (1963).

[3] J. O. Dimmock and A. J. Freeman, Phys. Rev. Letters 13, 750 (1964).

[4] A. J. Freeman, J. O. Dimmock, and R. E. Watson, Bull. Am. Phys. Soc. 10, 376 (1965).

[5] T. Nagamiya, K. Nagata, and Y. Kitano, Progr. Theoret. Phys. (Kyoto) 27, 1253 (1962).

[6] D. R. Behrendt, S. Legvold, and F. H. Spedding, Phys. Rev. 109, 1544 (1958).

[7] B. R. Cooper and R. J. Elliott, Phys. Rev. 131, 1043 (1963).

[8] H. Ehrenreich, H. R. Philipp, and D. J. Olechna, Phys. Rev. 131, 2469 (1963).

[9] G. S. Krinchik and G. M. Nurmukhamedov, Zh. Eksperim. i Teor. Fiz. 48, 34 (1965).

[10] D. H. Martin, S. Doniach, and K. J. Neal, Phys. Letters 9, 224 (1964).

[11] B. R. Cooper and H. Ehrenreich, Solid State Commun. 2, 171 (1964).

[12] B. R. Cooper, H. Ehrenreich, and L. Hodges, Proceedings of the International Conference on Magnetism, Nottingham, England, 1964 (The Institute of Physics and the Physical Society, University of Reading, Berkshire, England, 1965).

[13] B. R. Cooper, Phys. Rev. (to be published).

HIGH-SENSITIVITY PIEZOREFLECTIVITY

W. E. Engeler
General Electric Research Laboratory, Schenectady, New York

and

H. Fritzsche
Institute for Study of Metals, University of Chicago, Chicago, Illinois

and

M. Garfinkel and J. J. Tiemann
General Electric Research Laboratory, Schenectady, New York

(Received 18 May 1965)

This Letter describes an experimental technique that promises to be useful in the study of the energy band structure of solids. The technique is based on the fact that the optical reflectivity of a substance is in general changed by stress. The details of the changes depend upon the type of stress, the band structure of the material, and the wavelength of the light. These changes are most pronounced near the onset of direct interband transitions, and thus can yield information about these transitions. Since strain is a second-rank tensor, it is possible to obtain from single-crystal samples not only the position in energy of these transitions but also information about their location in the Brillouin zone. Further, the magnitude of the changes that are induced by a stress of known magnitude gives information about the deformation potentials of the bands involved. The potentialities of piezo-optics for yielding this type of detailed information have long been recognized.[1] In practice, however, the results have been severely limited by experimental difficulties. Previous static measurements of piezoreflectance[2] under uniaxial stress have required large ($\sim 10^{-2}$) sample strains. Since few materials may be strained this severely, this technique has been of limited usefulness. The experiment described below utilized oscillatory applied strain and synchronous detection at a frequency that is high in comparison with fluctuations in the photodetectors and other sources of instability. The resulting improvement in stability allows measurements to be made of relative reflectivity changes, $\Delta R/R$, as small as 5×10^{-6}. As a result, the method is useful for studying a wide range of solids. This sensitivity is similar to that reported by Seraphin and Hess[3] in measurements of electric-field-induced reflectivity changes in Ge. The ultimate sensitivity of this type of system is limited by photon shot noise. The sensitivity limit quoted above was in fact due to this source over much of the range covered. Even greater sensitivity could therefore be obtained if desired.

The experimental arrangement is shown schematically in Fig. 1. The sample to be studied is polished, and/or etched, and is mounted directly upon a piezoelectric transducer. An-

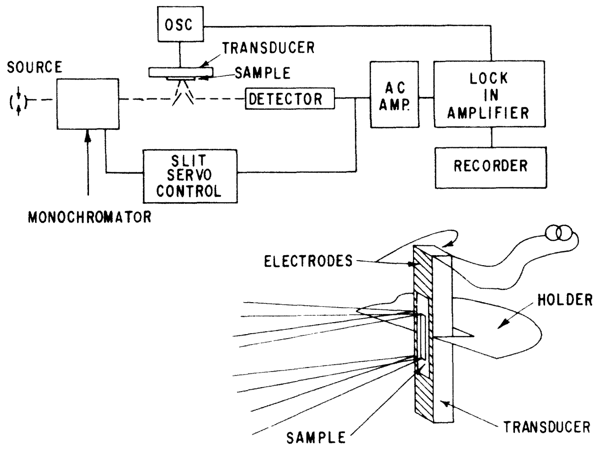

FIG. 1. Schematic representation of the experimental apparatus showing a block diagram of the optical and electrical components, and an insert drawing showing the sample and transducer assembly.

other procedure useful in the case of metals is to evaporate a film of the metal to be studied directly upon a polished face of the transducer. The samples are strained by driving the transducers at the desired frequency. The ac component of the reflected signal is detected synchronously with the driving voltage by means of the lock-in amplifier shown. The servo control of the monochromator slits adjusts the amount of light falling upon the photodetector so that the dc operating point of the detector is kept fixed. This automatically compensates for source-intensity fluctuations, and for wavelength variations of source intensity, detector sensitivity, and sample reflectivity. The ac output is thus directly proportional to $\Delta R/R$ independent of wavelength. For the experimental results shown below, the transducers were of the lead-zirconate-titanate type. The samples of Ge and Si were soldered to the transducer electrodes, and the Cu sample was evaporated directly onto a polished surface of the transducer. The operating frequency was approximately 1 kc/sec.

Figure 2 shows the results obtained for Si in the energy range 2.8-4.5 V, for Ge between 1.6 and 4.6 V, and for Cu between 1.9 and 5.6 V. Figure 3(a) shows the piezoreflectivity, $\Delta R/R$, in the vicinity of the direct edge of Ge. All these measurements were made with the samples at room temperature and with an applied dilatation of approximately 3×10^{-5} rms.

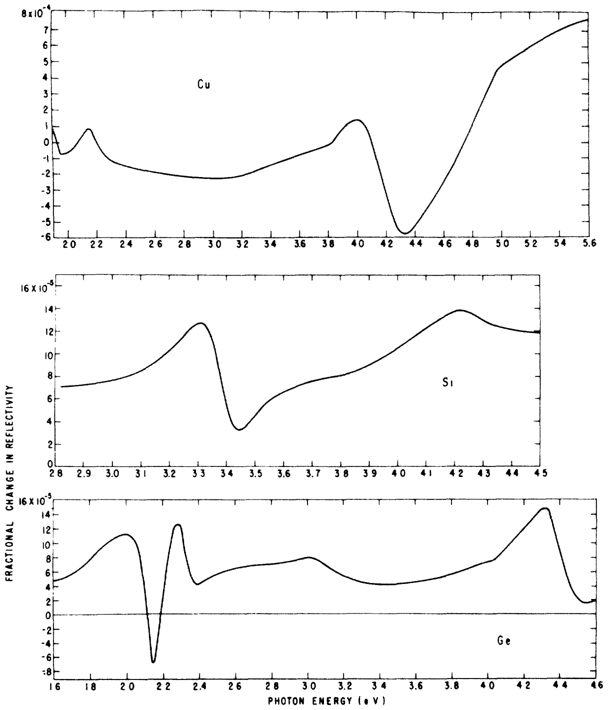

FIG. 2. Fractional change of reflectivity versus photon energy for Cu, Ge, and Si surfaces under a strain of approximately 3×10^{-5} rms, at room temperature. The zero is an instrument zero and should be considered arbitrary due to experimental uncertainties. Increasing R with compression plotted positive for Cu, and negative for Ge and Si.

In general, the reflectivity at normal incidence is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \qquad (1)$$

where n and k are the real and imaginary parts of the index of refraction, respectively. Although n and k are both simple numbers in unstressed cubic material, the index of refraction in stressed material can be different for different directions of polarization. Through Eq. (1), the piezoreflectivity is therefore dependent on the polarization direction, the directions of the stress, and the crystallographic directions. For cubic symmetry, in general, there are three independent complex constants[4] involved in this effect, and several different experiments are necessary to determine all of them. The data for Ge and Si, shown in Fig. 2, are observed to depend upon polarization direction and crystal orientation relative to the stress axis, but these aspects of the data are beyond the scope of this Letter, and will be reported elsewhere.

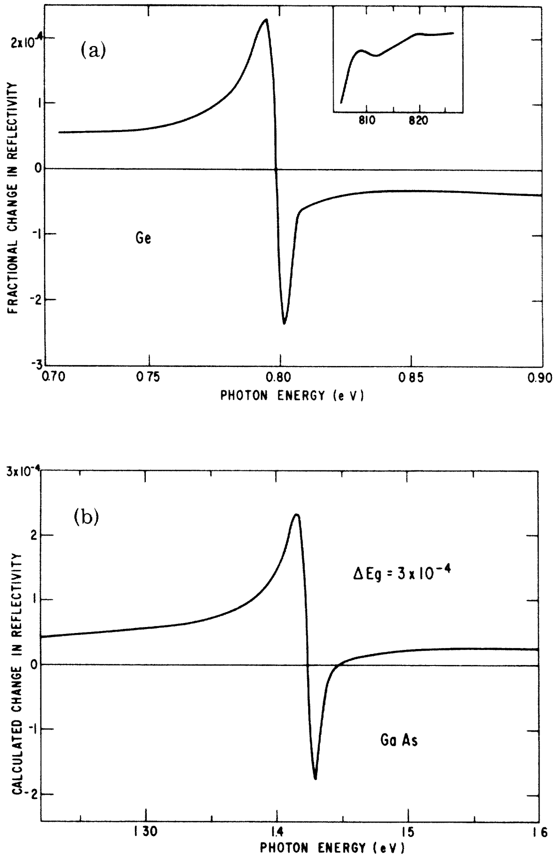

FIG. 3. (a) Fractional change of reflectivity versus photon energy for the Ge transition $\Gamma_{25'}$-$\Gamma_{2'}$ under a strain of approximately 3×10^{-5} rms, at room temperature. Arbitrary zero as in Fig. 2. Increasing $\boldsymbol{R}$ with extension plotted positive. (b) Fractional change of reflectivity versus photon energy calculated for GaAs assuming a rigid shift of the optical absorption spectra for the transition $\Gamma_{25'}$-$\Gamma_{2'}$ by 3×10^{-4} eV. (Calculated zero position.) Increasing $\boldsymbol{R}$ with extension plotted positive.

The general structure at the direct edge of Ge, as shown in Fig. 3(a), may be understood in terms of a simple deformation-potential[5] model. By means of the Kramers-Kronig relations[6] the relative reflectivity change can be related to a change of the absorption coefficient $\Delta\alpha(\omega)$:

$$\frac{\Delta R}{R} = A\frac{c}{\pi}\int_0^\infty \frac{\Delta\alpha(\omega')d\omega'}{[\omega'^2-\omega^2]} + \frac{c}{2\omega}B\Delta\alpha(\omega), \qquad (2)$$

where

$$A = 4\frac{(n^2-k^2-1)}{[(n+1)^2+k^2][(n-1)^2+k^2]}, \qquad (3)$$

and

$$B = 8nk/[(n+1)^2+k^2][(n-1)^2+k^2]. \qquad (4)$$

According to the deformation-potential model, both bands involved in an optical transition are shifted by an amount proportional to stress. To first order the absorption due to these transitions is shifted by an amount proportional to the difference of the deformation potentials of the two bands involved. This model has been applied to gallium arsenide, and the reflectivity changes in the vicinity of the direct edge resulting from a rigid shift of the absorption coefficient by 3×10^{-4} eV are show in Fig. 3(b). This calculation used the absorption coefficients as measured by Sturge[7] together with α's deduced from the reflectivity measurements of Philipp and Ehrenreich.[8] All of the changes shown in Fig. 3(b) result from the integral term of Eq. (2). For both germanium and GaAs at wavelengths close to their lowest direct edges, the quantity A is very much larger than B. The effects near these edges for both of these materials are therefore due solely to variations in n. Thus, aside from a difference in magnitude, the deformation-potential model predicts the same behavior for these two cases. The shift of 3×10^{-4} eV for the GaAs calculation corresponds to a net deformation-potential difference for the $\Gamma_{25'}$-$\Gamma_{2'}$ transition of 10 eV[9] and an applied rms dilatation of approximately 3×10^{-5}. A comparison of Figs. 3(a) and 3(b) shows that this simple model accounts for the gross features of the experimental results at this direct edge. The magnitude of the step between low and high energies and the additional structure near 0.81 eV, resolved in the insert of Fig. 3(a), was not obtained from the calculation.

In general the shape of the observed $\Delta R/R$ signal associated with a certain transition will depend on the type of transition and on the relative magnitudes of A and B in Eq. (2). These effects contribute to the complexity of the spectra exhibited in Fig. 2. In addition, several transitions may be nearly degenerate, further complicating the structure. A detailed analysis is required before a precise interpretation can be made.

For silicon near 3.4 eV two types of transitions are expected, $\Gamma_{25'}$-Γ_{15} and $L_{3'}$-L_1.[10] Each of these is a spin-orbit split doublet. For germanium near 2.2 eV the transitions $L_{3'}$-L_1 and

Λ_3-Λ_1 are expected.[11] The transition $\Gamma_{25'}$-Γ_{15} is expected near 3.0 eV. For both silicon and germanium additional structure is seen in the vicinity of 4.3 eV corresponding to the transitions X_4-X_1 and Σ_4-Σ_1.[10,11]

In copper, there is strong structure observed in the regions 1.9-2.3 V and 3.8-5.2 V, including abrupt changes in slope near 1.9, 3.8, and 4.9 eV. In the vicinity of 4.9 eV, transitions X_5-X_4, Σ_3-Σ_1, and between the two bands belonging to Σ_1 are expected. In the vicinity of 3.8 eV, the transition Σ_4-Σ_1 is expected, and the structure near 2 V is almost certainly related to transitions, from $Q+$, $Q-$, and Δ_5 to the Fermi surface.[12] Structure over this energy range has also been observed by reflectivity.[13]

This Letter describes piezoreflectance measurements 100 times more sensitive than previous results. This increase makes piezoreflectance measurements applicable to a much larger number of materials. The experimental data can be used to determine interband transition energies and deformation potentials, and can provide information about the location of the transitions in the Brillouin zone. The result of this experiment indicates that a similar peizo-optical transmission experiment is possible.

---

[1] H. R. Philipp, W. C. Dash, and H. Ehrenreich, Phys. Rev. 127, 762 (1962).

[2] Reference 1; U. Gerhardt, Phys. Letters 9, 117 (1964).

[3] B. O. Seraphin and R. B. Hess, Phys. Rev. Letters 14, 138 (1965).

[4] See, for example, J. F. Nye, Physical Properties of Crystals and Their Representation by Tensors and Matrices (Oxford University Press, New York, 1957).

[5] See, for example, R. W. Keyes, Solid State Phys. 11, 149 (1960).

[6] T. S. Moss, S. D. Smith, and T. D. F. Hawkins, Proc. Phys. Soc. (London) B70, 776 (1957).

[7] M. D. Sturge, Phys. Rev. 127, 768 (1962).

[8] H. R. Philipp and H. Ehrenreich, Phys. Rev. 129, 1550 (1963).

[9] R. Zallen and W. Paul, Phys. Rev. 134, A1628 (1964).

[10] H. Ehrenreich, H. Philipp, and J. C. Phillips, Phys. Rev. Letters 8, 59 (1962).

[11] D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962).

[12] B. Segall, Phys. Rev. 125, 109 (1962).

[13] H. Ehrenreich and H. R. Philipp, Phys. Rev. 128, 1622 (1962).

RELATIVISTIC ENERGY BANDS FOR LEAD BY THE RELATIVISTIC AUGMENTED PLANE-WAVE METHOD*

T. L. Loucks

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa

(Received 26 April 1965)

A method for calculating relativistic energy bands was recently developed by the author.[1] This method, which can be thought of as a generalization of the augmented plane-wave method,[2] was shown to give accurate results for a transition element in its first application to tungsten.[3] For that metal it was found that the spin-orbit splitting of degenerate levels as predicted by those calculations was in quantitative agreement with experimental results.

In this Letter we present the results of an *ab initio* energy-band calculation for lead using the relativistic augmented plane-wave (RAPW) method. These results are shown as solid curves in Fig. 1 and will be compared with the Fermi surface and band structure proposed by Anderson and Gold.[4-6] On the basis of de Haas-van Alphen measurements, these authors have given a very complete description of the Fermi surface using a pseudopotential interpolation scheme in which the spin-orbit interaction was taken into account. This parametrized Fermi surface was also found to be in very good agreement with experimental results obtained by other workers. The energy bands predicted by Anderson and Gold[6] are shown as dashed curves in Fig. 1 for comparison with the present results.

The theoretical Fermi energy was chosen such that intersections with the bands would give the best possible agreement with the parametrized Fermi surface; this surface was shown to very closely satisfy the requirement of equal hole and electron volumes. To facilitate comparison, the zero of energy for the RAPW bands has been shifted to bring the Fer-