The long-lived component was nevertheless clearly resolved from the shorter ones. For a discussion of the magnetic field effect on the positron lifetime spectra, we resort to the procedure employed previously in magnetic-quenching experiments.[7] One calculates the ratio R of the number of annihilations with field on and field off in a given interval of delayed-coincidence times chosen such that in this range the contribution of the short-lived components can be neglected.

The points in Fig. 3 show the results for the $C = 400$ ppm crystal pair. The intensity of the long-lived component so probed is clearly reduced by the static magnetic field. This suggests that the wave function of positrons trapped in Ca^{2+}-induced defects overlaps with an unpaired-spin component in the wave function of the crystal electrons near the trap.

The extent of the positron and unpaired-electron overlap can be deduced from the magnetic-quenching data as follows. A theoretical value of R can be calculated, according Ref. 7, with the overlap, expressed by the unpaired-electron density at the positron, $|\psi(0)|^2$, as the only adjustable parameter. With a least-squares-fitting procedure to our data one finds $|\psi(0)|^2 = (0.10 \pm 0.01)|\psi_{Ps}(0)|^2$, where $|\psi_{Ps}(0)|^2$ is the overlap in the ground state of positronium *in vacuo*. The resulting R is drawn in Fig. 3 (solid line). The quenching ratio R for positronium *in vacuo* is shown for comparison (dashed line).

The overlap with an unpaired electron is much more pronounced when positrons annihilate at the F centers in additively colored KCl crystals. Although the long lifetimes are nearly the same, one finds here a distinctly different quenching curve corresponding to $|\psi(0)|^2 = (0.29 \pm 0.04)|\psi_{Ps}(0)|^2$.[8] The significance of these differences as regards the electronic structure of the positron annihilation centers is under study.[9] It is apparent that magnetic quenching offers an effective method for differentiating in solids between long-lived positron states of different origins but of otherwise very similar annihilation characteristics.

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[*] Work supported by the Gruppo Nazionale di Struttura della Materia del CNR, Italy, and the U. S. National Science Foundation.

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[1] W. Brandt and H. F. Waung, Phys. Rev. B 3, 3432 (1971).

[2] F. H. Hsu, W. C. Mallard, and J. H. Hadley, Jr., in Proceedings of the Second International Conference on Positron Annihilation, Kingston, Ontario, 1971, p. 2.12 (unpublished).

[3] Cf., e.g., A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 20, p. 298.

[4] W. A. Sibley and J. R. Russell, J. Appl. Phys. 36, 810 (1965).

[5] E. Fermi and E. Teller, Phys. Rev. 72, 399 (1947).

[6] J. E. Turner, V. E. Anderson, and K. Lox, Phys. Rev. 174, 81 (1968), and references quoted therein.

[7] A. Bisi, A. Dupasquier, and L. Zappa, J. Phys. C 4, L311 (1971), and references quoted therein.

[8] A. Bisi, A. Dupasquier, and L. Zappa, J. Phys. C 4, L33 (1971).

[9] W. Brandt and A. Dupasquier, Bull. Am. Phys. Soc. 17, 284 (1972).

PHYSICAL REVIEW B VOLUME 6, NUMBER 8 15 OCTOBER 1972

Electric Field Effects in Optical and First-Derivative Modulation Spectroscopy

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(Received 10 April 1972)

The large selection of electroreflectance data available in the literature enables surface field effects on optical and first-derivative modulation spectra to be estimated for most materials. A method for doing this is presented.

Since the first experimental investigations of the electroreflectance effect, it has been recognized that surface electric fields in a semiconductor or insulator could influence the values of optical "constants," determined either directly by means of normal- or non-normal-incidence techniques or indirectly by means of first-derivative techniques.[1] Yet in most such experimental measurements, electric field effects either have been ignored altogether, or else their neglect has been justified by extrapolating null results obtained in a limited spectral range on one material to a series of spectra on different materials.[2] While field effects are negligible in many optical measurements, this is by no means always the case. In this comment, we wish to emphasize that the known systematics and voluminous amount of published experimental electroreflectance data can prove extremely useful either in justifying this neglect in specific situations, or in providing criteria which show when field effects must be taken into account. Thus, electroreflectance spectra themselves can often be used directly to justify field independence within a given accuracy, and therefore substantiate (or disprove) in a simple way the independence which otherwise must be assumed.

We consider first experiments in which the complex index of refraction or the complex linear dielectric function is determined directly. Here electric field effects are qualitatively similar to those caused by surface roughness and contaminating films. The latter effects are well known in these measurements, and considerable effort has gone into compensating or eliminating them.[3] Since by optical constants we mean those parameters describing the intrinsic optical properties of a material in its unperturbed state, the effect of a surface electric field clearly has implications for these measurements. For example, in a reflectivity measurement, the reflectivity can be represented as

$$R = R_0 + \Delta R(\vec{\mathcal{E}}) = R_0[1 + \Delta R(\vec{\mathcal{E}})/R_0] \ , \tag{1}$$

where R_0 is the intrinsic reflectivity and $\Delta R(\vec{\mathcal{E}})$ is the error term. We take the error term to be explicitly a function of the surface field $\vec{\mathcal{E}}$, although other perturbations such as strain or photoreflectance effects could be included as well, with the appropriate generalization of the subsequent discussion. The error term $\Delta R(\vec{\mathcal{E}})/R_0$ is that quantity measured directly in electroreflectance experiments; thus its general limits, magnitude, and characteristics can be inferred from electroreflectance data. These data show typically that $\Delta R(\vec{\mathcal{E}})/R_0$ ranges from less than 10^{-6} in regions away from critical points in the joint density of states to of the order of 0.001–0.005 in the vicinity of critical points for semiconducting crystals with no strong exciton binding,[4] to of the order of 0.005–0.02 in the vicinity of the fundamental absorption edge or exciton resonances in crystals with strong or readily observable exciton line spectra,[5] to upwards of 0.10 in ferroelectric or nearly ferroelectric materials.[6] For example, in electroreflectance spectra for Ge or Si, $\Delta R/R$ does not exceed 0.004 in magnitude even for the strong E_0 and E_1 transitions.[5,7] For ZnO, a semiconductor with a strong exciton-absorption line near the fundamental absorption edge, electroreflectance spectra are much larger,[8] which is consistent with the field-induced change of 5% in the reflectivity observed by Hoffman.[9] Thus, in an accurate measurement of the dielectric function of a material, the first step should be to estimate from its experimental electroreflectance spectrum whether field effects are large enough in the spectral region of interest to affect the desired accuracy of the measurement. If large enough, then either the field will have to be measured and the reflectivity data corrected by the appropriate electroreflectance line shape, or else the field will have to be eliminated at the experimental level by any of a number of techniques now available.

Field effects in first-derivative measurements can also be estimated from experimental electroreflectance data. In terms of the previous notation the line shape obtained in a wavelength-modulation measurement will be

$$\begin{aligned} \frac{1}{R}\frac{dR}{dE} &= \frac{1}{R_0+\Delta R}\frac{d}{dE}(R_0+\Delta R) \\ &= \frac{1}{R_0}\frac{dR_0}{dE} - \frac{\Delta R}{R_0^2}\frac{dR_0}{dE} + \frac{1}{R_0}\frac{d}{dE}(\Delta R) \ , \end{aligned} \tag{2}$$

where the first term is the unperturbed spectrum and the remaining two terms describe field-induced errors. The first error term is usually much less than the second, as can be shown by the noting that

$$\frac{1}{R_0}\frac{d}{dE}(\Delta R) \sim \frac{\Delta R}{R_0\Gamma} \ , \tag{3}$$

where Γ is the broadening parameter. Equation (3) follows because electroreflectance structure widths tend to be of the order of the broadening energy of the transition.[10] This effective amplification factor E/Γ means that field effects will generally be much more important in derivative rather than direct spectroscopy. For example, Welkowsky and Braunstein (WB) observe a response $(1/R)dR/dE \sim 0.60\ \text{eV}^{-1}$ for the E_1 transition of Ge in wavelength-derivative spectroscopy.[2] Using the maximum signal $\Delta R/R \sim 0.002$ and the observed broadening $\Gamma \sim 60$ meV for these transitions,[7] we calculate the correction term [Eq. (3)] to be $\sim 0.03\ \text{eV}^{-1}$ in the worst case or about 5% of the amplitude of the wavelength-modulation spectrum. It is unlikely that WB were able to maintain a significant difference in field over an extended period of time using a KCl-electrolyte solution, which is probably why no field effect was reported. However, it is evident that the calculated field effect in this situation *is* large enough to be detected, even though typical accuracy requirements may not warrant a detailed correction. We note that the E_1 transition probably represents a practical dividing line below which excitonic effects are strong and field corrections are mandatory, and above which ER signals are weak and such corrections can probably be ignored.

These effects should be investigated experimentally. Optical and first-derivative modulation spectra ideally should be run on semiconductor samples in which the surface field is zero. If this is not possible, then the surface field should be determined by some independent measurement such as field-effect conductance, photovoltaic response, or surface capacitance. The results of such a carefully surface-controlled experiment may very well assist in interpretations of dielectric function and first-derivative modulation spectra to the extent that these spectra are even more informative than they are at present.

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[1] M. Cardona, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Vol. 11; B. O. Seraphin, Surface Sci. 8, 399 (1967); 13, 136 (1969).

[2] Specific examples of the complete neglect of these effects will not be cited, since this neglect is standard practice. One example of a partial treatment of these effects can be found in M. Welkowsky and R. Braunstein, Phys. Rev. B 5, 497 (1972).

[3] H. E. Bennett and J. M. Bennett, in *Physics of Thin Films*, edited by G. Hass and R. E. Thun (Academic, New York, 1967), Vol. 4.

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

[5] M. Cardona, K. L. Shaklee, and F. H. Pollak, Phys. Rev. 154, 696 (1967).

[6] A. Frova and P. J. Boddy, Phys. Rev. Letters 16, 688 (1966).

[7] D. E. Aspnes and A. Frova, Phys. Rev. B 2, 1037 (1970); S. Koeppen, P. Handler, and S. Jasperson, Phys. Rev. Letters 27, 265 (1971).

[8] The electroreflectance spectrum for ZnO in Ref. 5 is anomalously small due to the small modulation voltage (20 mV rms) used in its measurement.

[9] B. Hoffman, Z. Physik 219, 354 (1969).

[10] D. E. Aspnes and J. E. Rowe, Solid State Commun. 8, 1145 (1970); Phys. Rev. B 5, 4022 (1972).

PHYSICAL REVIEW B VOLUME 6, NUMBER 8 15 OCTOBER 1972

Phonon Conductivity of Doped and Undoped Silver Chloride*

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(Received 10 January 1972)

It is shown in the present work that the transverse phonons make a major contribution towards thermal transport in pure and doped AgCl crystals. Experimental dispersion curves as obtained by Vijayaraghavan *et al.* are used in obtaining the limits and phonon velocities of the different conductivity integrals. A theoretical estimate of dislocation densities is also obtained from the phonon scattering strengths due to dislocations.

Recently Chau and Klein[1] proposed a two-group velocity model for the theoretical calculation of the thermal conductivity of silver chloride. With this model they explained the experimental results from samples of doped and undoped silver chloride quite successfully up to 40 °K. For higher temperatures this model predicted lower values than those obtained from the experimental results. In this model there is no distinction between longitudinal phonons and transverse phonons. This distinction is, however, desirable in view of the difference in the dispersive nature and the different relaxation times for the two types of phonons. Such a provision exists in the Holland model[2] or the model of Sharma *et al.* (referred to as SDV)[3,4] of phonon conductivity. In the present note we have used the Holland model to explain the phonon conductivity results[1] on pure as well as on doped AgCl for three different concentrations of NaCl, which is used as the doping material. The values of the velocities and the limits of the conductivity integrals for the different polarization branches are calculated from the experimental dispersion curves, measured by Vijayaraghavan *et al.*[5] in the appropriate direction and are given in Table I.

For pure crystals, the total relaxation rate is taken to be $\tau^{-1} = \tau_B^{-1} + \tau_i^{-1} + \tau_{pp}^{-1}$. Here τ_B^{-1} and τ_i^{-1} are the relaxation rates due to the scattering of phonons by boundary and isotopes, respectively, and are given by[6,7]

$$\tau_B^{-1} = v/1.12\,d\eta, \quad \tau_i^{-1} = A\omega^4, \quad A = (\Omega_0/4\pi v^3)S_0^2 ,$$

where v is the average group velocity of phonons and the rest of the quantities are defined else-