Experimental Evidence for Exciton Effects at M_1 Saddle-Point Singularities in a Layer Structure

M. Grandolfo, F. Somma, and P. Vecchia
Physics Laboratory, Istituto Superiore di Sanità, Rome, Italy
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Strong experimental evidence is reported for the importance of the metamorphism of critical points in the temperature-modulated reflectance spectra of a strongly anisotropic material such as GaS. The experimentally observed line shape, identified as due to transitions associated with an M_1 critical point located in the point Q of the Brillouin zone, has been quite well interpreted as arising from an unique critical point built up from M_1 and M_0 singularities (bidimensional approximation), taking into account the different effect of the modulating parameter. The good agreement between the experimental points and the curve calculated on the basis of the Toyozawa's theory provides strong evidence that the exciton model describes (also in a bidimensional crystal) the effect of the Coulomb interaction upon the direct interband transitions above the fundamental edge quite well.

Among the various types of many-body interactions neglected in the one-electron approximation, the electron-hole interaction is known to play one of the most important roles. Many modifications in the one-electron spectra have been ascribed by several authors to the existence of a significant contribution of the electron-hole Coulomb interaction (exciton effects) to the experimentally observed optical-modulation line shapes.[1] The theoretical problem of excitonic effects was first treated by Toyozawa *et al.*[2] by replacing the Coulomb potential by a finite-range potential; they were able to predict between the critical-point nature and the exciton coupling strength the existence of a cyclic relationship whose main effect is the mixing (in the neighborhood of a critical point M_j) of the M_j line shape and that which one would expect for an M_{j+1} critical point (one defines $M_4 \equiv M_0$). A similar result has been recently obtained extending the Slater-Koster "contact" interaction to an approximate theoretical treatment of exciton effects at general critical points in electroreflectance.[3] Experimental evidence is available so far in the E_1 region for electroreflectance,[3] thermoreflectance,[4] piezoreflectance,[5] and wavelength-modulated[6] reflectance spectra of materials having the diamond and the zinc-blende structures.

In this paper we report for the first time strong experimental evidence for the importance of the metamorphism of critical points in the temperature-modulated reflectance spectra of a strongly anisotropic material such as GaS, whose optical properties can be conveniently studied in a two-dimensional model.[7]

The measurements presented were taken at liquid-nitrogen temperature in the energy range of 3.6–4.4 eV and at near-normal incidence using unpolarized light. The experimental arrangement that has been used is the standard one in the technique of temperature-modulated solid-state spectroscopy.[8] Measurements were performed on hexagonal GaS samples; the crystals were in platelet form and specimens suitable for reflectivity measurements were readily obtained by cleavage using a razor blade.

From the point of view of the chemical bond, the trigonal coordination of the nearest neighbors in GaS can be interpreted by a model in which the s, p_x, and p_y orbitals participate in forming the same type of strong coplanar bonds as those in graphite. Bassani and Pastori Parravicini[9] evaluated the band structure of graphite, GaS, and GaSe by using the tight-binding approximation in a semiempirical way, while Kamimura and Nakao[10] derived the detailed structures of the conduction and valence bands of GaS and GaSe near the Fermi energy, pointing out the existence of two-dimensional pair bands corresponding to transitions between π bands. From the evaluated band structures, strong peaks appear in the joint density of states of the three materials, in correspondence to transitions at the point Q of the Brillouin zone, owing to the fact that in this band scheme Q is a saddle point. These peaks remain in $\epsilon_2(0, \omega)$ and correspond to the peaks obtained from absolute-reflectivity experiments both in graphite,[11] and GaS and GaSe.[12] In Fig. 1 we show, in the region of interest, the spectral dependence of the fractional changes of the real and imaginary parts of the dielectric constant $\Delta\epsilon_1$ and $\Delta\epsilon_2$ as derived by a Kramers-Kronig analysis of our experimental data of fractional change of reflectance $\Delta R/R$. The values of ϵ_1 and ϵ_2 used in our computation were obtained by processing the known reflectivity spectra of GaS.[13]

It is well known that in the two-dimensional approximation, which consists in neglecting the interaction between different layer planes, the critical points reduce to those of the M_0 and M_1 type, giving

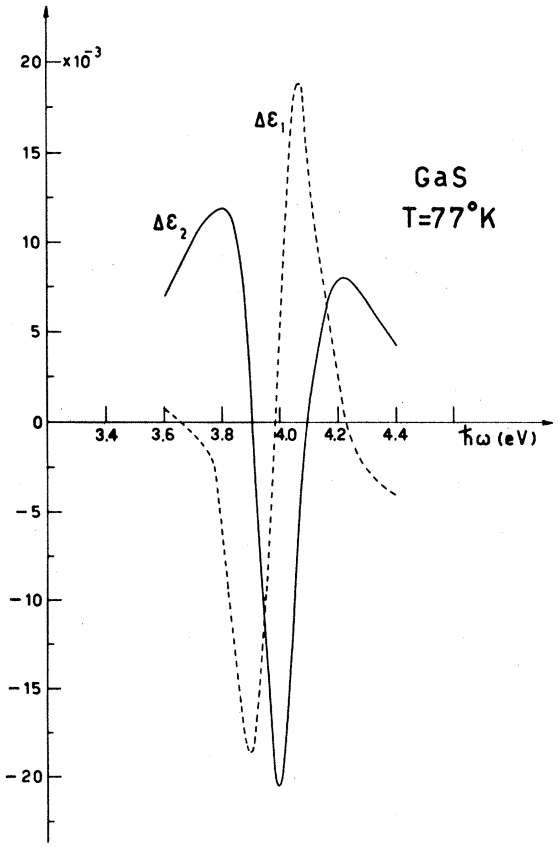

FIG. 1. Fractional changes of the real (dashed line) and imaginary parts (solid line) of the dielectric constant of GaS, obtained from the Kramers-Kronig transformation of the experimental spectrum of $\Delta R/R$.

rise, respectively, to step and logarithmic singularities in the joint density of states.[7] Experimental results previously obtained by temperature modulating the optical constants of graphite[14] suggested that for this material the effect of temperature is mainly to shift the M_0 critical points and to broaden the M_1 saddle-point singularity occurring at Q in the Brillouin zone. An attempt was then made to fit the line shape of $\Delta\epsilon_2$ with the following expression:

$$\Delta\epsilon_2 = \frac{(\hbar\omega - E_c)^2 - \frac{1}{4}\Gamma^2 - \frac{1}{2}\Gamma\Delta\Gamma}{[(\hbar\omega - E_c)^2 + (\frac{1}{2}\Gamma + \Delta\Gamma)^2][(\hbar\omega - E_c)^2 + \frac{1}{4}\Gamma^2]}\,\Delta\Gamma\,, \tag{1}$$

representing, as in the case of graphite, a symmetrical broadening without shift of the Lorentzian line describing the M_1 logarithmic singularity. Here E_c, Γ, and $\Delta\Gamma$ are the energy of the critical point, its broadening parameter, and the Γ temperature modulation, respectively. The result of the fit of Eq. (1) is so poor (Fig. 2) that we are led to recognize the failure of the one-electron model in correctly interpreting the observed line shape. Figure 2 shows a comparison of our experimental results with the following theoretical curves: (i) that obtained by interpreting the observed line shape as due to only an M_1 saddle-point singularity symmetrically broadened by temperature modulation, and (ii) that resulting from application of the Toyozawa theory. This latter curve is obtained assuming the observed structure as arising from a unique critical point built up from the metamorphism of the two possible Van Hove singularities (M_1 and M_0), taking into account that the effect of temperature, as observed in the case of graphite, is to shift one of the critical points (M_0) and to broaden the other one (M_1) because of the electron-phonon interaction. The lifetime broadening of the M_0 point has been introduced through a convolution integral,[15] using a Lorentzian parameter Γ. The only adjustable parameters were the energy position E_1 and the lifetime broadening parameter Γ. The calculated curve with no exciton interaction gives the values $E_1 = 3.998 \pm 0.001$ eV and $\Gamma = 0.211 \pm 0.001$ eV, while the curve obtained by mixing the line shapes expected for the M_1 and M_0 critical points, taking into account the different effects of the modulating perturbation, gives $E_1 = 3.993 \pm 0.001$ eV and $\Gamma = 0.289$

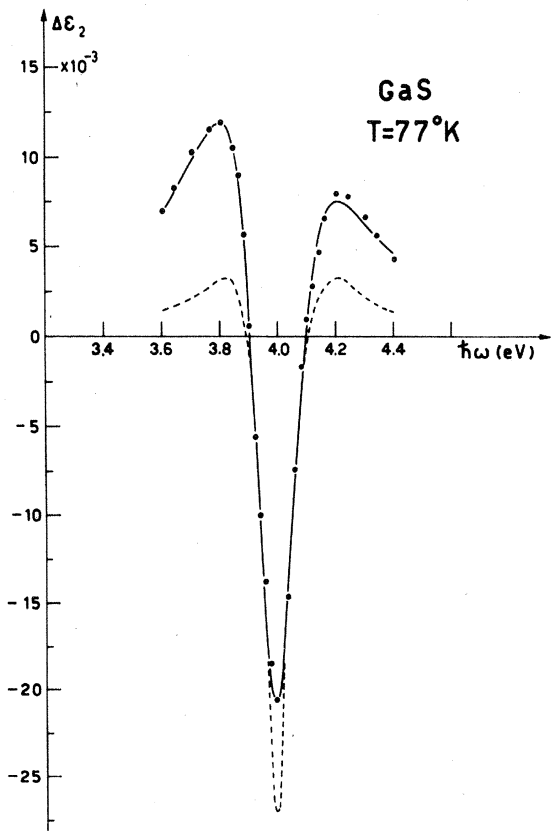

FIG. 2. A comparison of theoretical curves excluding (dashed line) and including (solid line) the electron-hole interaction with the experimental data (•) of Fig. 1. The solid line has been evaluated assuming that the effect of temperature is to shift the M_0 critical point and to broaden the other one (M_1), as in the case of Ref. 14.

± 0.001 eV. The M_0-point contribution to the resulting line shape is about 25%.

We feel that the good agreement (Fig. 2) between the experimental points and the curve calculated on the basis of the metamorphism of critical points provides strong evidence that the exciton model describes quite well (also in a bidimensional crystal) the effect of the Coulomb interaction upon the direct interband transitions above the fundamental edge. Further work is now in progress to show the presence of such an effect in GaSe.

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Dynamical Theory of the Large Polaron: Fock Approximation

D. Matz and B. C. Burkey
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650
(Received 18 November 1970)

A Green's-function equation-of-motion analysis of the large polaron is presented. Existing theories for the ground-state energy and effective mass are obtained from a nondiagonal form of the Fock approximation to the electron self-energy. A connection between the usual canonical transformation techniques and the Green's-function approach is given explicitly. The effects of vertex corrections and translational invariance are examined in the context of these results.

I. INTRODUCTION

The problem of the large polaron has received considerable attention in the past.[1-4] There remain, however, a number of unanswered theoretical questions which arise when one attempts to make predictions that can be verified experimentally. For a small electron-phonon coupling constant α, the polaron ground-state energy can be obtained from perturbation theory,[1,3-6] and has the form

$$E_0 = -\alpha - 0.0159\alpha^2 - O(\alpha^3) .$$

For large α, the ground-state energy has the form[1-4]

$$E_0 = -a_0\alpha^2 - a_1\alpha^0 - O(\alpha^{-2}) .$$

Thus, as indicated by Larsen,[7] polaron perturbation theory must have a finite radius of convergence. This implies a critical coupling constant α_c such that for $\alpha > \alpha_c$ the polaron spectrum develops internal structure. The experimental verification of the internal structure would be facilitated by a theory which predicts α_c, the internal-energy spectrum, and the lifetimes of the states.[8] A Green's-function equation-of-motion approach to the polaron problem should be appropriate because of its ability to handle dynamic effects and because it permits a systematic accounting of electron-phonon correlations by the use of Feynman graphs. Such a theory does not exist. On the other hand, existing polaron theories cannot be easily applied to these questions, partly because of mathematical complexities[9,10] and partly because of inherent limitations.[8,11-18] For example, Feynman's theory predicts $\alpha_c = 0$. The theories of Pekar[11] and Bogoliubov and Tiablikov[12] (referred to as PBT and reviewed by Allcock[13]) are adiabatic theories and therefore