PHYSICAL REVIEW B VOLUME 14, NUMBER 2 15 JULY 1976

Optical absorption and *s* and *p* phase shifts of virtual-bound-state alloys

D. Beaglehole
Victoria University of Wellington, Private Bag, Wellington, New Zealand

(Received 23 February 1976)

The results of optical studies of the nonmagnetic virtual-bound-state alloys CuNi, AuNi, AgPd, and AuPd are summarized. The importance of *s* and *p* phase shifts of the impurity potential is emphasized, and the results are reanalyzed in terms of an expression for the frequency-dependent relaxation time which includes *s*, *p*, and *d* phase shifts and is consistent with the Friedel sum rule. CuNi appears anomalous. The various limitations of the theoretical expressions are discussed and it is suggested that CuNi may be understood if the effects of spin fluctuations are considered.

Transition-metal impurities in noble-metal hosts form virtual-bound-state alloys. The basic properties of these states—the width and position in the conduction band—can be inferred indirectly from resistivity and specific-heat data, but can be obtained directly from spectroscopic studies. In this paper those optical studies to date which provide a complete set of data are summarized. The studies cover the alloys CuNi, AuNi, AgPd, and AuPd. To obtain an interpretation of the data which is consistent with the Friedel sum rule it is necessary to include the *s* and *p* phase shifts of the impurity potential in addition to the customary *d* phase shift, so that an expression for the frequency-dependent relaxation time which includes all three phase shifts is developed, and the data reanalyzed. Using all three phase shifts it is possible to fit not only the optical-absorption line shape, which depends upon the variation of the relaxation time relative to its dc value, but also its absolute magnitude. The procedure works well for the last three of the alloys above, but is not good for the CuNi alloy. The paper discusses effects which go beyond the free-electron treatment and suggests that spin fluctuations may well be needed to explain the CuNi results.

I. VIRTUAL-BOUND-STATE PROPERTIES

Friedel[1] considered the scattering of free conduction electrons by the impurity potential and showed that a resonance in the $l=2$ d component of the potential gives rise to a localized impurity state with a Lorentzian density of d states given by

$$n_d(E) = (10/\pi)\{\Delta/[(E_d - E)^2 + \Delta^2]\}\,. \tag{1}$$

The states are centered at energy E_d, with a half width at half height of Δ; the impurity spin states are degenerate in the nonmagnetic alloys. The d phase shift is given by

$$\delta_2(E) = \tan^{-1}[\Delta/(E_d - E)]\,. \tag{2}$$

An estimate of the s and p phase shifts can be obtained once δ_2 is known using the Friedel sum rule

$$Z = (2/\pi)(\delta_0 + 3\delta_1 + 5\delta_2)_{E_F}\,, \tag{3}$$

where Z is the excess impurity charge and the phase shifts are evaluated at the Fermi level. In terms of the phase shifts the impurity resistivity is given (with n_i impurity atoms, and n conduction electrons per unit volume) by

$$\rho = (m^*/ne^2)(n_i/\tau_i)\,, \tag{4}$$

where

$$\frac{\hbar}{\tau_i} = \frac{4}{\pi n_s}\sum_l (l+1)\sin^2(\delta_l - \delta_{l+1})_{E_F}\,. \tag{5}$$

The phase shifts and n_s (the conduction-electron density of states for both spins per atom) are evaluated at the Fermi level. Considering only the $l=2$ component

$$\frac{\hbar}{\tau_i} = \frac{20}{\pi n_s}\sin^2\delta_2 = 2\Delta\frac{n_d(E_F)}{n_s(E_F)}\,. \tag{6}$$

Anderson's[2] approach to the virtual-bound-state alloys coupled the conduction s electrons with the impurity d potential through the matrix element V_{sd}. The lifetime for the scattering of conduction electrons by both impurity d states is

$$\hbar/\tau = 2\pi V_{sd}^2 n_d(E_F)\,, \tag{7}$$

while the lifetime for the decay of the d state into both spin states of the conduction band is

$$2\Delta = 2\pi V_{sd}^2 n_s(E_d)\,. \tag{8}$$

Eliminating $2\pi V_{sd}^2$ from these two equations again gives Eq. (6), if $n_s(E)$ varies little between E_F and E_d.

Optical studies use photon energies $\hbar\omega$ to excite conduction electrons within a range of $\hbar\omega$ below the Fermi level to states within a range of $\hbar\omega$ above the Fermi level. It is thus plausible that the relaxation time for a frequency ω should be the average of the relaxation times over a range $-\hbar\omega$ to $+\hbar\omega$ about the Fermi level. Considering only the d component, we define

$$\hbar/\tau_{i(E)} = (20/\pi n_s)\sin^2\delta_2(E)\,, \tag{9}$$

so that

$$\hbar/\tau_{i(\omega)} = \langle \hbar/\tau_{i(E)}\rangle_{\pm\hbar\omega}\,, \tag{10}$$

which leads to

$$\frac{\hbar}{\tau_{i(\omega)}} = \frac{\hbar}{\tau_{i(0)}}\,\frac{\langle n_d(E)\rangle}{n_d(E_F)}\,\pm\hbar\omega \tag{11}$$

or

$$\frac{\hbar}{\tau_{i(\omega)}} = \frac{4}{\pi n_s}\,\frac{5\Delta}{2\hbar\omega} \times\left(\tan^{-1}\frac{\hbar\omega-(E_F-E_d)}{\Delta}+\tan^{-1}\frac{\hbar\omega+(E_F-E_d)}{\Delta}\right). \tag{12}$$

It has been shown (Beaglehole[3]) that these expressions for the frequency-dependent relaxation time when used with the Drude conductivity give a high-frequency absorption which is just the same as that calculated by more sophisticated models of Caroli[4] and Kjollerstrom.[5] A more detailed study of the virtual-bound-state dielectric constant (Beaglehole[6]) shows that complete consistency requires a modified conduction-electron effective mass.

The expression (11) for the frequency-dependent relaxation time can be generalized to include the s and p phase shifts if one returns to Eq. (5). We have

$$\frac{\hbar}{\tau_{i(\omega)}} = \frac{4}{\pi n_s}\left\langle \sum_l (l+1)\sin^2(\delta_l-\delta_{l+1})\right\rangle_{\pm\hbar\omega}. \tag{13}$$

The energy dependence is in δ_2 while δ_0 and δ_1 are assumed to be energy independent. The averaging in Eq. (13) leads to

$$\frac{\hbar}{\tau_{i(\omega)}} = \frac{4}{\pi n_s}\Bigg[\sin^2(\delta_0-\delta_1)+2\sin^2\delta_1+\frac{\Delta}{2\hbar\omega}(5-4\sin^2\delta_1)\left(\tan^{-1}\frac{\hbar\omega-(E_F-E_d)}{\Delta}+\tan^{-1}\frac{\hbar\omega+(E_F-E_d)}{\Delta}\right) - \frac{\Delta}{2\hbar\omega}\sin 2\delta_1\ln\left(\frac{[\hbar\omega-(E_F-E_d)]^2+\Delta^2}{[\hbar\omega+(E_F-E_d)]^2+\Delta^2}\right)\Bigg] \tag{14}$$

[compare with Eq. (12) for the d component above].

II. OPTICAL STUDIES

The alloys discussed here have been studied by independent workers with good consistency of results. Those we summarize are CuNi (Drew and Doezema,[7] Kunz and Beaglehole[8]); AuNi (Lao, Doezema, and Drew,[9] Bassett and Beaglehole[10]); AgPd (Callender and Schnatterly,[11] Lafait[12]); AuPd (Theye,[13] Lafait[12]). In the region $\omega\tau \gg 1$ the imaginary part of the dielectric constant may be written

$$\epsilon_2 = \frac{\omega_p^2}{\omega^3\tau}+\epsilon_{2ib} = \frac{\omega_p^2}{\omega^3}\left(\frac{1}{\tau_p}+\frac{c}{\tau_i}\right)+\epsilon_{2ib}\,. \tag{15}$$

ω_p is the alloy plasma frequency, c is the impurity concentration, and ϵ_{2ib} is the interband absorption. Thus the change in ϵ_2 on alloying $\Delta\epsilon_2$ in the region below the host interband absorption is directly related to $1/\tau_i$ and the interband absorption involving the impurity state. Assuming a constant matrix element ω_d for interband excitation of the impurity d states into conduction-electron states and for conduction states into empty impurity states, $\Delta\epsilon_2$ may be written (Kjollerstrom[5]):

$$\Delta\epsilon_2 = \frac{\omega_p^2}{\omega^3}\,\frac{c}{\tau_i}+\frac{c\omega_d^2}{\omega^2}\,\pi\hbar\omega\langle n_d(E)\rangle_{\pm\hbar\omega}\,. \tag{16}$$

The authors above[7-13] have fitted their experimental results to this expression, using only the d contribution to $\hbar/\tau_i$. Four parameters were adjusted, $\hbar/\tau_i(0)$, Δ, E_d, and ω_d. Callender and Schnatterly and Lao, Doezema, and Drew have varied V_{sd}^2 rather than $\hbar/\tau_i(0)$, but from Eqs. (7) and (8) this is an entirely equivalent procedure. The experimental data extend to energies much less than E_F-E_d, where $\langle n_d\rangle_{\pm\hbar\omega}\sim n_d(E_F)$, so $\Delta\epsilon_2$ in this region fixes $\hbar/\tau_i(0)$. The peak in $\Delta\epsilon_2$ fixes E_F-E_d, while the relative increase in ϵ_2 over its value with a constant $\hbar/\tau_i$ determines Δ. The variation above E_F-E_d determines ω_d. Thus the four parameters are essentially independent. Table I displays the various experimental results. Values for E_d and Δ obtained by different workers are in good agreement—only for AgPd is Lafait's value for Δ much larger than Callender and Schnatterly's, but a trend to larger Δ for concentrations above 3 at.% was observed by Callender and Schnatterly which would account for this difference. $\hbar/\tau_i(0)$ values are more variable, the variation possibly arising from the difficulty in determining alloy concentrations accurately.

In Table I two further quantities derived from the experimental values of Δ and E_d are shown, the value of $\hbar/\tau_i(0)$ derived from Eq. (6), and the value of $\delta_0+3\delta_1$ derived from Eq. (3) ($Z=9$ for the

TABLE I. Values of the four virtual-bound-state parameters and the derived $\delta_0+3\delta_1$ for different alloys.

	c	$\hbar/\tau_i(0)$ [a] (eV)	Δ (eV)	E_F-E_d (eV)	$\hbar\omega_d$ (eV)	δ_2	$\delta_0+3\delta_1$	$\hbar/\tau_d(0)$ [b]
CuNi Ref. 8	0.01	0.713	0.224	0.78	2.5	2.862	−0.173	1.617
Ref. 7	0.01	1.13 (1.27)	0.25	0.72	1.4	2.807	0.102	2.288
AuNi Ref. 10	<0.02	1.475	0.115	0.476	7.4	2.897	−0.348	1.529
Ref. 9	0.02	1.305 (1.16)	0.108	0.47	2.9	2.916	−0.443	1.305
AgPd Ref. 11	<0.03	0.361 (0.348)	0.242	2.086	3.6	3.026	−0.993	0.396
Ref. 12	0.075	0.47	0.38	2.18	2.8	2.969	−0.708	0.877
AuPd Ref. 13	0.095 − 0.040	0.30 (0.275)	0.15	1.60	2.4	3.048	−1.103	0.228
Ref. 12	<0.06	0.42	0.195	1.65	1.71	3.024	−0.983	0.359

[a] Where two values are shown, the experimental value is that in parentheses, to which a correction has been applied to compensate for effective mass changes not taken into account by the authors.

[b] Calculated from Eq. (6) using values n_s given in Table II.

alloys here). It can be seen that for all alloys except CuNi the values of $\hbar/\tau_i(0)$ are reasonably close to the experimental values but for these alloys the sum rule suggests that there are sizable *s* and *p* phase shifts which have been neglected in the analysis. For CuNi, $\delta_0+3\delta_1$ is small, but the calculated value of $\hbar/\tau_i(0)$ is almost a factor of 2 greater than the experimental value; *s*, *p*, and *d* phase shifts interfere in the relaxation-time equation and smaller values for $\hbar/\tau_i(0)$ could be obtained if *s* and *p* phase shifts were included in the analysis. Thus the optical data have been reanalyzed using the expression for $\hbar/\tau_{i(\omega)}$ which includes all three phase shifts [Eq. (14)], choosing δ_0, δ_1, and δ_2 (through E_d and Δ) so that the sum rule is consistently satisfied.

The parameters δ_0, E_d, Δ, and ω_d have been varied until the new theoretical fit is in least-squares agreement with the "experimental" curves calculated from the average of the parameters for each alloy in Table I (for AgPd in view of the concentration dependence of Δ mentioned above an "experimental" curve was calculated using Callender and Schnatterly's values only). The fitting was carried out over a range from zero to a maximum energy corresponding to that used by the authors in deriving the experimental values. Figures 1–4 compare the experimental curves with the new theoretical results, while Table II lists the values of Δ and E_d and the phase shifts resulting from the new analysis. The line shape depends upon the signs of the phase shifts, so these are determined in the fitting procedure.

In those alloys where $\hbar/\tau_i(0)$ was close to the value calculated from the *d* phase shift alone, that is for all except CuNi, the new procedure has increased Δ and decreased E_d, reducing δ_2 slightly. For CuNi Δ has been reduced drastically, and while now a value for $\hbar/\tau(\omega)$ of the right magnitude is obtained, the new line shape is sufficiently different from the experimental curve that the amounts of *s* and *p* phase shifts required to produce the reduction in magnitude must be considered unreasonable. It is interesting to note that the Pd impurity produces *s* and *p* phase shifts of almost the same size in the two Ag and Au hosts.

III. DISCUSSION

While Sec. II has shown that *s* and *p* phase shifts can contribute in a significant way to the frequency-dependent relaxation time, CuNi remains an anomalous alloy. The optical line shape for CuNi

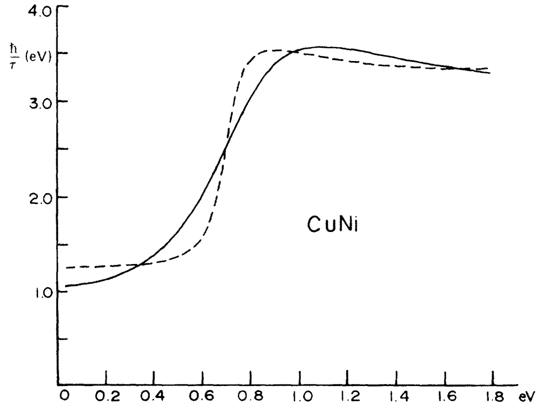

FIG. 1. Comparison of the experimental frequency-dependent relaxation time for CuNi (full line) with the least-squares theoretical fit found using the *s*, *p*, and *d* phase-shift analysis (dashed line).

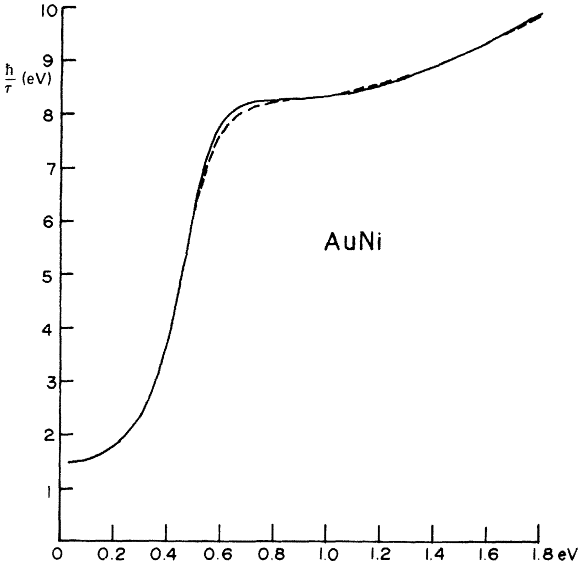

FIG. 2. Comparison of the experimental frequency-dependent relaxation time for AuNi (full line) with the least-squares theoretical fit found using the s, p, and d phase-shift analysis (dashed line).

could perhaps be obtained by a value of Δ as low as 0.2 eV, but the experimental value for $\hbar/\tau_i(0)$ is still much lower than what would then be given by a consistent admixture of s and p phase shifts. The analysis has been based upon the model of free electrons scattered by a central potential. The limitations of the model with particular reference to the anomalous CuNi results will be discussed here.

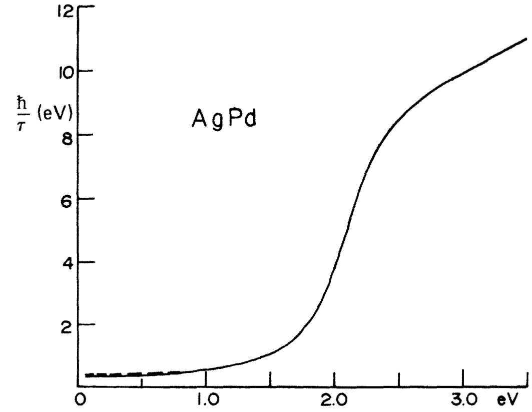

FIG. 3. Comparison of the experimental frequency-dependent relaxation time for AgPd (full line) with the least-squares theoretical fit found using the s, p, and d phase-shift analysis (dashed line). Theoretical curve for the most part lies on top of the experimental curve.

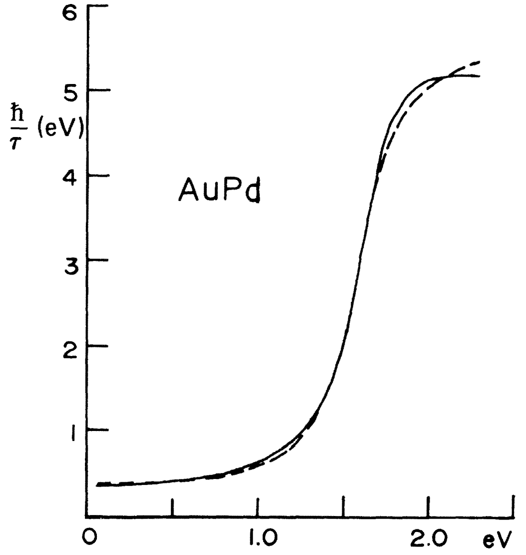

FIG. 4. Comparison of the experimental frequency-dependent relaxation time for AuPd (full line) with the least-squares theoretical fit found using the s, p, and d phase-shift analysis (dashed line).

A. Anisotropy of the relaxation time

The Friedel expression considers τ_i a function of energy only, neglecting any wave-vector dependence for the conduction electrons. In fact, de Haas–van Alphen studies (Springford,[14] Coleridge[15]) have shown that τ_i can vary considerably over the Fermi surface. Coleridge suggests that belly orbits in CuNi scatter more strongly than neck orbits by a factor of 2. The effective relaxation time in the region $\omega\tau \gg 1$, where $1/\tau_i(0)$ is determined optically, is proportional to an integral over the Fermi surface of the form

$$\left(\frac{1}{\tau_i}\right)_{\mathrm{hf}} \propto \int \frac{v_k}{\tau_k}\, ds$$

and thus weights the strongly scattering extended belly surfaces. Thus since the free electron equation should estimate the relaxation time for the belly surfaces fairly well, it is clear that anisotropy cannot explain the low experimental values.

B. Lorentzian line shape

Theoretical calculations for CuNi based upon Green's-function approaches by Harris,[16] Reidinger,[17] and Cook and Smith[18] have shown that while real impurity states cannot be expected to be exactly Lorentzian in detail, they are not greatly different. The impurity states of these authors appear to fall more rapidly on the lower-energy side $E < E_d$. Since the optical absorption involves

TABLE II. Values of E_d, Δ, and the phase shifts obtained from *s,p,d* analysis.

	Experimental parameters						*s,p,d* analysis					
	$(\hbar\omega)_{\max}$ (eV)	$\hbar/\tau_i(0)$ (eV)	E_F-E_d (eV)	Δ (eV)	$\hbar\omega_d$ (eV)	n_s $(\text{eV})^{-1}$	E_F-E_d (eV)	Δ (eV)	$\hbar\omega_d$ (eV)	δ_0	δ_1	δ_2
CuNi	1.8	1.01	0.75	0.237	1.95	0.30	0.710	0.062	1.49	−0.682	−0.151	3.055
AuNi	1.8	1.39	0.473	0.111	5.15	0.244	0.469	0.112	5.12	−0.247	−0.050	2.907
AgPd	3.5	0.361	2.086	0.242	3.60	0.214	2.065	0.254	3.45	−0.278	−0.227	3.019
AuPd	2.3	0.361	1.625	0.172	2.05	0.244	1.574	0.186	2.34	−0.247	−0.245	3.024

an average over the impurity density of states, it is not sensitive to small departures from Lorentzian. For example, Cook and Smith calculated from their theoretical density of states an optical line shape which lies close to the experimental curve (allowing for differences between their value of E_d and the experimental value). Note that Cook and Smith have omitted the factor 2 in Eq. (6) in determining the relaxation time, and the theoretical calculations point up the same anomaly as found experimentally for CuNi.

Lao, Doezema, and Drew[9] have noted the anomalous properties of CuNi, and have suggested that an interaction between the host and impurity *d* states should lead to a non-Lorentzian impurity state. They argue that this interaction would be more important in CuNi than AuNi because the impurity state lies closer to the host *d* states in the copper alloy. They have suggested that the *sd* matrix element should be energy dependent with the form

$$V_{sd}^2(E)=V_{sd}^2(E_F)[1+\alpha(E-E_d)]$$

fitting their CuNi data (using the *d* phase shift alone) with a value of α of −0.56. In this approach Δ becomes a function of energy, varying by a factor of 2 between E_F and E_d. The resulting impurity state is steepest on the high-energy side $E>E_d$ which is not evident in the theoretical calculations referred to above. Their proposed interaction should be even more important for AuPd where the impurity lies closest to the host *d* state, but there is no sign of the anomaly there. Thus the case for an energy-dependent interaction of the magnitude suggested by these authors is unconvincing.

C. Spin fluctuations

Spin fluctuations of the type discussed by Rivier and Zuckermann[19] which involve extensions of the Friedel and Anderson theories beyond the Hartree-Fock approximation also modify the Lorentzian line shape. The effects depend upon the relative sizes of the Kondo temperature T_K and Δ and become important when $kT_K<\Delta$. Model density of states have been calculated by Zlatic, Gruner, and Rivier.[20] For $T<T_K$ and $kT_K<\Delta$, the Lorentzian impurity state splits into two humps lying symmetrically about E_d. This is a tendency towards spin splitting of the impurity state, but since T is less than T_K, with no magnetic effects. Estimates for T_K for CuNi and AuNi alloys (Daybell and Steyert[21]) lie in the range 1000 to 2000°K corresponding to energies between 0.086 and 0.172 eV, so the inequality $kT_K<\Delta$ will be satisfied by CuNi but not by AuNi alloys. Estimates of T_K for the Pd alloys do not appear available. The density of states of each hump will be approximately half that of the full Lorentzian. Thus it seems reasonably likely that the optical studies on CuNi are probing only the higher-energy hump of the modified impurity density of states. Its smaller density of states will provide less scattering but essentially the same optical line shape. Further spin-fluctuation model calculations with parameters appropriate to CuNi would be valuable.

ACKNOWLEDGMENT

The author is indebted to Dr. A. B. Kaiser for descriptions of the spin-fluctuation effects and other helpful discussions.

---

[1] J. Friedel, Nuovo Cimento Suppl. 7, 287 (1958).
[2] P. W. Anderson, Phys. Rev. 124, 41 (1961).
[3] D. Beaglehole, Phys. Lett. A 40, 209 (1972).
[4] B. Caroli, Phys. Kondens. Mater. 1, 346 (1964).
[5] B. Kjollerstrom, Philos. Mag. 19, 1207 (1969).
[6] D. Beaglehole, J. Phys. F 5, 657 (1975).
[7] H. D. Drew and R. E. Doezema, Phys. Rev. Lett. 28, 1581 (1972).
[8] C. Kunz and D. Beaglehole (unpublished).
[9] B. Y. Lao, R. E. Doezema, and H. D. Drew, Solid State

Commun. 15, 1253 (1974).

[10] M. Bassett and D. Beaglehole, J. Phys. F (to be published).

[11] A. B. Callender and S. E. Schnatterly, Phys. Rev. B 7, 4385 (1973).

[12] J. Lafait, C. R. Acad. Sci. (Paris) 279, B59 (1974).

[13] M. L. Theye, Thesis (University of Paris, 1968) (unpublished).

[14] M. Springford, Adv. Phys. 20, 493 (1971).

[15] P. T. Coleridge, J. Phys. F 5, 1317 (1975).

[16] R. Harris, J. Phys. C 3, 172 (1970).

[17] R. Reidinger, J. Phys. F 1, 392 (1971).

[18] C. L. Cook and P. V. Smith, J. Phys. F 4, 1344 (1974).

[19] N. Rivier and M. J. Zuckermann, Phys. Rev. Lett. 21, 904 (1968).

[20] V. Zlatic, G. Gruner, and N. Rivier, Solid State Commun. 14, 639 (1974).

[21] M. D. Daybell and W. A. Steyert, Rev. Mod. Phys. 40, 380 (1968).