large g shifts (departures from the free-electron g value) observed, the unusually large oscillator strengths for such forbidden transitions, and the apparently large spin-orbit coupling. These arguments also hold for the $[K]^0$ centers. One might speculate on other models where the hole is less localized, and indeed some evidence for such delocalization has been noted.[3,4] A satisfactory model should not only explain the large g shifts and oscillator strengths, but also the transition energies, the large half-widths of the optical bands, and the low thermal stability of the centers.

In addition, the model should be able to account for transitional changes in the properties of the centers due to changes in either the ionic size of the impurity or the host lattice. An examination of the properties of the trapped-hole centers upon such changes was an objective of the present study. Our results and that of previous workers are summarized in Table II. There appears to be a correlation between the optical-absorption energy, the annealing temperature, and the g shifts for the centers. As the host crystals are changed, regular trends are observed. Host crystals with heavier cations give centers which are less stable and have lower optical-absorption energy and larger g shifts. Thus, one can conclude that the depth of the potential well for the centers is decreasing in a more or less regular manner with the host lattice, but no single-parameter model has been found.

There are some unexpected features arising from the $[K]^0$ centers. Potassium is expected to behave differently than lithium or sodium because of its larger ionic size. Indeed, it is surprising that it fits at all into the oxide lattice. The properties of the $[K]^0$ centers do not fit into a progression corresponding to the ionic size of the monovalent alkali-metal ions. Rather, the optical-absorption energy, g shifts, and annealing temperatures of the $[K]^0$ centers in CaO and SrO are intermediate between those of the $[Li]^0$ and $[Na]^0$ centers in these same hosts.[3,4] Hence, as one proceeds down the series of alkali substitutional ions in the same host, no simple trend exists. Another rather unusual result is that, whereas in the case of the $[Li]^0$ and $[Na]^0$ centers[2-4] the hyperfine structures are more clearly resolved when the magnetic field is perpendicular to the axis of the center rather than parallel, the reverse is true for $[K]^0$ centers. This suggests that for the $[K]^0$ centers, unlike the $[Li]^0$ or $[Na]^0$ centers, the isotropic and anisotropic parts of the hyperfine tensor a and b, respectively, have the same sign and are roughly equal in value.

---

†Research conducted at Oak Ridge National Laboratory was sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

*Present address: Physics Department, Rice University, Houston, Tex.

[1] A. E. Hughes and B. Henderson, in *Defects in Crystalline Solids*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972), and references therein.

[2] O. F. Schirmer, J. Phys. Chem. Solids 32, 499 (1971).

[3] H. T. Tohver, B. Henderson, Y. Chen, and M. M. Abraham, Phys. Rev. B 5, 3276 (1972).

[4] M. M. Abraham, Y. Chen, J. L. Kolopus, and H. T. Tohver, Phys. Rev. B 5, 4945 (1972).

[5] After E. Sonder and W. A. Sibley, in Ref. 1.

[6] M. M. Abraham, C. T. Butler, and Y. Chen, J. Chem. Phys. 55, 3752 (1971).

[7] W. E. Hagston, J. Phys. C 3, 1233 (1970).

PHYSICAL REVIEW B VOLUME 7, NUMBER 6 15 MARCH 1973

Thermo- and Elasto-optic Parameters of NaF and Their Implications for Light Scattering from Second Sound

Dieter W. Pohl and S. E. Schwarz*
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland

(Received 15 May 1972; revised manuscript received 24 November 1972)

The intensity of light scattered from second sound is estimated for the case of NaF, the only dielectric crystal in which second sound is presently known. For this purpose we have measured the thermo-optic coefficient $(\partial n/\partial T)_p$ of NaF between 300 and 10 °K as well as the elasto-optic tensor at room temperature. The scattered intensity is calculated to be less than the value predicted by the Landau–Placzek ratio, and in fact the Rayleigh component is expected to vanish entirely at one particular temperature (approximately 34 °K).

I. INTRODUCTION

The phenomenon of second sound, i. e., wavelike propagation of entropy fluctuation, has recently attracted considerable theoretical[1] and experimental[2] interest, in part because of its recent detection in a normal dielectric crystal, NaF.[3] Most experimental work up to now has been performed with the heat-pulse technique.[4] It has been pointed out[5] that light scattering could also be a powerful tool for the investigation of second sound, since it would supply direct information on the dispersion and damping of these waves. Scattering of light from second sound in liquid helium has already been demonstrated, for instance by Pike *et al.*,[6] who observed that the Rayleigh scattering peak was transformed into a doublet resembling the Brillouin doublet, but with a smaller frequency difference. The frequency shift provides a measurement of the velocity of second sound, while the width of the peaks is related to the damping of the second-sound wave. The purpose of the present work is to evaluate the feasibility of optical-second-sound scattering experiments in the case of NaF, which as yet is the only normal dielectric crystal in which second sound is known to exist.

A difficulty that is encountered in many conventional light-scattering experiments arises from the extremely low intensity of the scattered light. In a second-sound experiment, the scattered intensity depends on the square of the amplitude of the temperature fluctuations and also on the coupling coefficient, which is proportional to $\partial n/\partial T$. (This partial derivative is to be taken with appropriate constraints, as discussed in Sec. III.) Both of these quantities would be expected to be very small at low temperatures. If one wishes to go farther and obtain an actual quantitative estimate of the scattering, however, it is necessary to know the relevant thermo-optic and elasto-optic parameters, which we have therefore measured. Although it is by no means a foregone conclusion *a priori*, we find that in fact nature has adjusted to parameters of NaF in such a way that conventional detection of scattered light will be extremely difficult. This does not rule out the possibility of all second-sound scattering experiments. On the contrary, experiments in which artificially generated (as opposed to spontaneously existing) second sound is used are possible. The data presented here will be useful in the design and interpretation of such experiments. We have also found that an interesting cancellation of the components of the scattering should occur, so that the Rayleigh scattering from NaF will actually vanish at one particular temperature.

II. THERMO- AND ELASTO-OPTIC PARAMETERS

In order to estimate the scattered intensity, we have measured the temperature dependence of the refractive index $(\partial n/\partial T)_p$ for NaF between 10 and 300 °K as well as the elasto-optic coefficients p_{ij} at room temperature. To our knowledge this relevant information has not previously been available.[7] The values of $(\partial n/\partial T)_p$ and also of the linear thermal expansion $\alpha_l(T)$ were obtained from two sets of interferometric measurements, one employing a Jamin interferometer with a NaF sample in one beam, the other a Fabry–Perot etalon made from a NaF crystal. The optical-path-length variations with temperature in the two interferometers are given, respectively, by

$$\frac{\Delta L_{\text{opt}}}{L\Delta T}\bigg|_J = \left(\frac{\Delta n}{\Delta T}\right)_p + \alpha_l\,(n-1) \tag{1a}$$

and

$$\frac{\Delta L_{\text{opt}}}{L\Delta T}\bigg|_{\text{FP}} = \left(\frac{\Delta n}{\Delta T}\right)_p + \alpha_l n\,. \tag{1b}$$

Simultaneous solution of these two equations allows determination of $(\partial n/\partial T)_p$ and α_l. Crystals of NaF, made from Merck "Suprapur" NaF, were supplied by Karl Korth *oHG*, Kiel, and a Spectra-Physics model-130 He-Ne laser was used as light source for the interferometry.

The measurements are shown in Fig. 1. As temperature decreases, α_l varies from 30 to 0.01 $\times 10^{-6}$ °K^{-1}. Its low-temperature behavior follows approximately a T^3 law. As a check, good agreement is obtained with the values of α_l previously measured by James and Yates[8] in the range 40–270 °K. The value of $(\partial n/\partial T)_p$ decreases from -12 to -0.002×10^{-6} °K^{-1}, again approximately following a

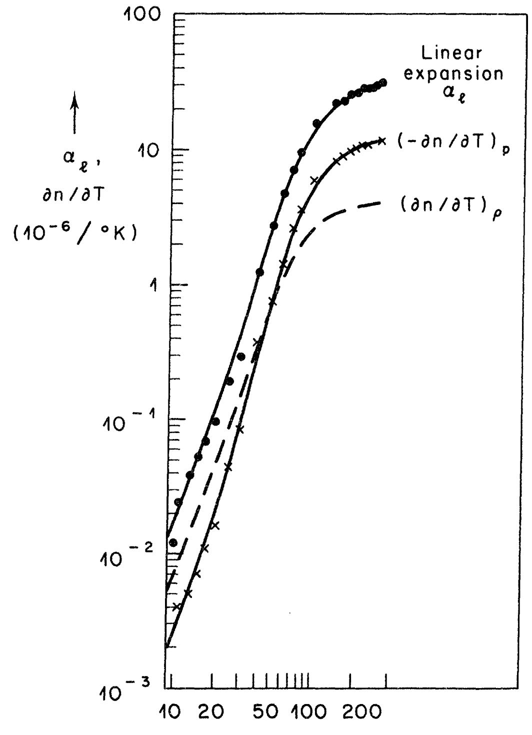

FIG. 1. Measured values of $(\partial n/\partial T)_p$ and linear expansion coefficient of NaF vs temperature. The calculated $(\partial n/\partial T)_\rho$ is also shown.

T^3 law in the low-temperature region. The small values of the coefficients at the lowest temperatures make accurate measurements difficult. The errors in $(\partial n/\partial T)_p$ and α_l are estimated at 10% above 20 °K, and 30% at 10 °K. The elasto-optic coefficients p_{11} and p_{12} were determined statically at room temperature, again using a Jamin interferometer, and checked by measurement of the stress-induced birefringence (p_{44} was measured by birefringence only). Low-temperature measurements of the elasto-optic coefficients were not made, since a strong temperature dependence is not expected. The measured values $p_{11}=0.08$, $p_{12}=0.02$, $p_{44}=-0.03$ are thought to be accurate within 20%. Using these values, it is possible to decompose $(\partial n/\partial T)_p$ into a density-dependent part representing the influence of particle density on polarizability, and a density-independent part $(\partial n/\partial T)_\rho$ representing the temperture dependence of the polarizability per particle. It is readily shown that $(\partial n/\partial T)_\rho$ is given by

$$\left(\frac{\partial n}{\partial T}\right)_\rho=\left(\frac{\partial n}{\partial T}\right)_p+\frac{n^3\alpha_l(p_{11}+2p_{12})}{2}\ . \qquad (2)$$

The temperature dependence of $(\partial n/\partial T)_\rho$ is also shown in Fig. 1. It will be noted that $(\partial n/\partial T)_\rho$ is positive. Thus the contribution of $(\partial n/\partial T)_\rho$ counteracts that of $(\partial n/\partial \rho)_T\,(\partial \rho/\partial T)_p$, in contradiction to all other known alkali halides.[9]

In Table I our experimental results at room temperature are compared with data taken from the literature[10] for LiF, NaCl, KCl, and KBr. We see that there is a tendency for the parameters of these alkali halides to vary more or less in accordance with the molecular weight of the compounds. The thermo-optic coefficients of NaF, however, are exceptional. In this connection it should be noted that the refractive index of NaF also has an exceptional value, the lowest of all the alkali halides and in fact one of the lowest of all transparent crystals.

III. ESTIMATION OF BRILLOUIN AND RAYLEIGH INTENSITIES

In order to estimate the strength of Rayleigh (or second-sound) scattering we begin with an estimation of the Brillouin-scattered intensity. The Rayleigh-scattered intensity can then be obtained by means of the thermodynamic relationship between the two modes.[11] Let us consider an incident light wave traveling in the [010] direction of a cubic crystal, and pressure (first-sound) and entropy (second-sound) fluctuations propagating in the [100] direction. Following the analyses of Benedek and Fritsch[12] and Durand and Pine,[13] we obtain, for the total power dP_B of the Brillouin-scattered light scattered into a solid angle $d\Omega$ (integrated over the whole spectral line) close to forward direction ($\cos\theta \simeq 1$),

$$\frac{dP_B}{P_0\, d\Omega}=\pi^2 kTln^8\,\frac{p_{12}^2}{2\lambda_0^4\rho v_1^2}\ . \qquad (3)$$

Here P_0 is the power incident on a sample of length l, ρ is the density, and kT is the thermal energy to which the intensities of the thermodynamic fluctuations are proportional. As is usual, only longitudinal phonons are considered here. Values of $dP_B/P_0\,d\Omega$ calculated from Eq. (6) for a 1-cm NaF crystal are shown as a function of temperature, in Fig. 2. The linear dependence on temperature arises from constant coupling between first sound and light and the linear decrease of the amplitude of thermodynamic fluctuations. The scattering rate in Eq. (3) is nearly independent of both the scattering angle θ and of the polarization direction of the incident wave because a small value of θ has been assumed. The observation of scattering at such a small angle will of course be complicated by the correspondingly small angle of acceptance (perhaps[14] $\Delta\Omega=10^{-4}$ sr) and by stray light.

The intensity relation between the Rayleigh or

TABLE I. Thermo- and elasto-optic parameters of alkali halides at room temperature.

Compound	$\left(\frac{\partial n}{\partial T}\right)_p$ (10^{-6} °K^{-1})	$\left(\frac{\partial n}{\partial T}\right)_\rho$	α_l	p_{11}	p_{12}	p_{44}	n	r
LiF	-16^a	-3.6^a	32.6^b	$\sim 0.02^c$	0.13^c	-0.064^c	1.39^d	-0.35
NaF	-12	$+5.0$	31.0	0.08	0.20	-0.030	1.32^d	$+0.48$
NaCl	-37^a	-8.0^a	39.5^b	0.11^c	0.15^c	-0.010^c	1.52^d	-0.50
KCl	-36^a	-17^a	36.7^b	0.22^c	0.16^c	•••	1.47^d	-0.41
KBr	-40^a	-1^a	38.1^b	0.22^c	0.17^c	-0.26^c	1.54^d	-0.06

[a] E. E. Havinga and A. J. Bosman, Phys. Rev. 140, A292 (1965).

[b] J. G. Collins and G. K. White, in *Progress in Low-Temperature Physics*, edited by C. J. Porter (North-Holland, Amsterdam, 1964), Vol. IV, p. 450.

[c] Landolt-Börnstein, *Zahlenwerte und Funktionen*, edited by K. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1966), Neue Serie, Gruppe III, Band 1.

[d] R. P. Lowndes and D. H. Martin, Proc. R. Soc. Lond. A 308, 473 (1969).

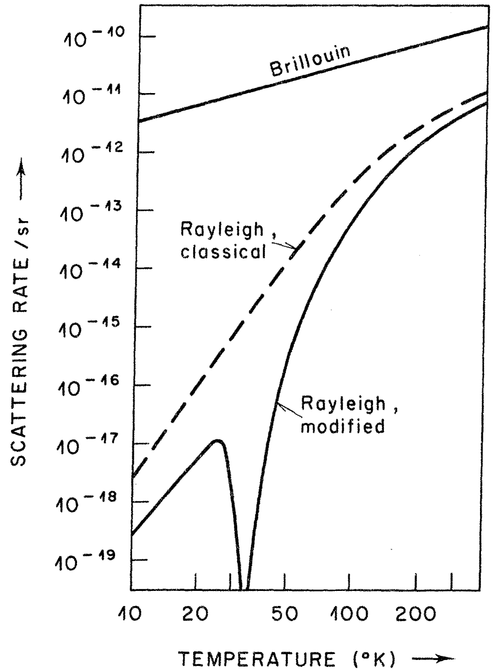

FIG. 2. Predicted scattering rates for NaF. The "classical" curve is obtained using the Landau–Placzek ratio, while the "modified" curve results from the corrected ratio of Wehner and Klein.

second-sound component and the Brillouin-scattered light was first investigated by Landau and Placzek,[11] who obtained

$$R_{\mathrm{LP}} = \frac{C_p - C_v}{C_v} \simeq \frac{c_{11}\, T (3\alpha_t)^2}{C_p} \qquad (4)$$

under the assumption $(\partial n/\partial T)_\rho = 0$. ($c_{ij}$ is the elastic tensor; C_p and C_v are the specific heats.) Equation (4) has been enlarged upon by several workers.[15] Wehner and Klein[16] have recently considered Rayleigh scattering in solids. They introduce modifications to the Landau–Placzek ratio arising from the nonzero value of $(\partial n/\partial T)_\rho$ and from the fact that transverse strain must vanish in a plane longitudinal wave, while instead transverse stress is present. Consequently, the effective value of $(\partial n/\partial T)$ lies between the values of $(\partial n/\partial T)_p$ and $(\partial n/\partial T)_\rho$. These considerations result in a modified Landau–Placzek ratio[16]

$$R_{\mathrm{WK}} = R_{\mathrm{LP}}(1 - r)^2, \qquad (4a)$$

where r is given by

$$r = -\frac{1}{\alpha_t}\,\frac{1}{1 + 2\, c_{12}/c_{11}}\,\frac{(\partial n_1/\partial T)_\rho}{(\partial n_1/\partial u_2)_T}\,. \qquad (5)$$

Here n_1 and u_2 are components of the refractive index and strain tensors, respectively. Wehner and Klein have calculated values of the ratio R_{WK} for a number of substances at room temperature. However, because of missing experimental data on crystal parameters, they were not able to substitute low-temperature data, nor were they able to treat the interesting case of NaF. Using our measurements of $(\partial n/\partial T)_p$ and p_{ij}, we have obtained R_{WK} as a function of temperature, as shown in Fig. 3. (The behavior of the uncorrected Landau–Placzek ratio is also shown, for comparison.) Multiplying $dP_B/P_0\, d\Omega$ from Eq. (3) by R_{WK} gives the estimated Rayleigh scattering as a function of temperature. These results are shown along with the Brillouin curve, previously discussed, in Fig. 2. (For comparison, the product $R_{\mathrm{LP}} \times dP_B/P_0\, d\Omega$ is also shown in Fig. 2.) In obtaining these curves the known[17] weak temperature dependence of the elastic constants was taken into account, but the values of the elasto-optic coefficients were assumed to be independent of temperature. The specific heat C_p was taken from the literature.[18,19]

For every material considered by Wehner and Klein at room temperature, it was found that $R_{\mathrm{WK}} > R_{\mathrm{LP}}$. However in NaF the opposite is true and as a result the expected scattering is even smaller than the already small value which would be calculated from the Landau–Placzek ratio. In fact there should be a zero of the Rayleigh scattering at a temperature near 34 °K. Physically, at this particular temperature the contributions to the effective $\partial n/\partial T$ from $(\partial n/\partial \rho)_T\,(\partial \rho/\partial T)_p$ and $(\partial n/\partial T)_\rho$ are equal and opposite, so that cancellation occurs.

It should be recalled that these results are based on the assumption that the elastic or thermal waves propagate in the [100] direction. Somewhat different values of R_{WK} would be found for other direc-

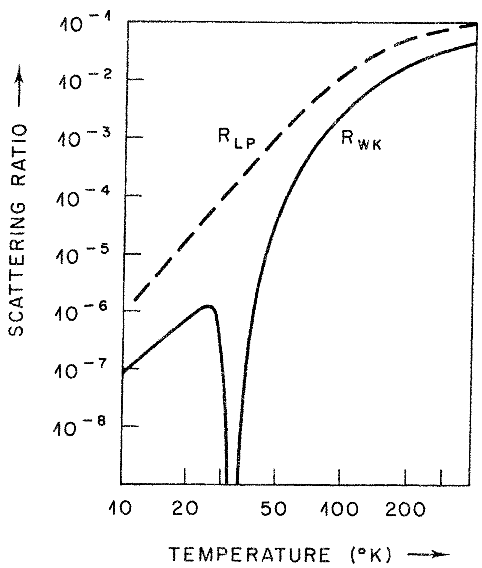

FIG. 3. Temperature dependences of the classical Landau–Placzek and corrected Wehner–Klein ratios for the case of NaF.

tions in the crystal.

In a scattering experiment one could apply a visible incident beam of perhaps 1 W, and a detector might collect the scattered radiation in 10^{-4} sr.[14] This would imply a scattering from spontaneous thermal fluctuations of around 10^{-15} W at room temperature, and of about $10^{-21}-10^{-22}$ W at the temperature of the second-sound window. Even at room temperature such a signal level is probably too small for heterodyne detection. It might barely be detectable by means of photon counting, but scattering from imperfections or impurities would tend to mask it and increase the difficulty of an observation. The $10^{-21}-10^{-22}$-W signal we estimate for scattering from thermal second sound is so small as to make its observation by any means quite unlikely. In other dielectric crystals, (or in other directions in NaF), the situation should be similar, although the scattering might conceivably be one or two orders of magnitude more intense due to more favorable values of the parameters entering Eqs. (3)–(5). We conclude that alternative techniques for study of second sound in crystals should be emphasized. For example, instead of relying upon spontaneous thermal fluctuations, one could artificially excite the requisite second-sound waves by means of an external sinusoidally excited heat transducer, as has already been done in the case of liquid helium.[20] Another possible technique is to apply a pair of coherent light waves with frequency difference ν_2, meeting inside the bulk of an absorbing crystal at a small angle, so as to produce a moving "thermal grating." Such "forced" thermal or second-sound waves will be many orders of magnitude more intense than those appearing spontaneously, and thus can be detected by optical-scattering techniques. We are presently making use of the latter technique and intend to present our results in a later publication.

ACKNOWLEDGMENTS

The technical assistance of V. Irniger is gratefully acknowledged. The authors thank R. K. Wehner and R. Klein for valuable discussions.

---

*Permanent address: Electrical Engineering Dept., University of California, Berkeley, Calif.

[1] For a comprehensive bibliography see, for example, G. Niklasson, Ann. Phys. (N. Y.) 59, 263 (1970); C. P. Enz, Ann. Phys. (N.Y.) **46**, 114 (1968); R. Klein and R. K. Wehner, Phys. Kondens. Mater. **10**, 1 (1969).

[2] T. F. McNelly, S. J. Rogers, D. J. Channin, R. J. Rollefson, W. M. Goubeau, G. E. Schmidt, J. A. Krummhansl, and R. O. Pohl, Phys. Rev. Lett. 224, 100 (1970); H. E. Jackson, C. T. Walker, and T. F. McNelly, Phys. Rev. B 3, 26 (1970).

[3] (a) E. H. Jackson and C. T. Walker, Phys. Rev. B **3**, 1428 (1971); (b) S. J. Rogers, Phys. Rev. B 3, 1440 (1971); cf. also the literature cited in these references.

[4] For a comprehensive bibliography see, for example, J. M. Andrews, Jr. and W. P. Strandberg, Proc. IEEE **43**, 523 (1966).

[5] A. Griffin, Phys. Lett. **17**, 208 (1965); R. H. Enns and R. R. Haering, Phys. Lett. 21, 534 (1966).

[6] E. R. Pike, J. M. Vaugham, and W. F. Vinen, Phys. Lett. A 30, 373 (1969); cf. also G. Winterling and T. J. Greytak (unpublished).

[7] H. W. Hohls [Ann. Phys. (Leipz.) **29**, 433 (1937)] gives a value $(dn/dT)_p = 1.6 \times 10^{-5}\,°\mathrm{K}^{-1}$ at $\approx 320\,°\mathrm{K}$.

[8] B. W. James and B. Yates, Philos. Mag. **12**, 253 (1965).

[9] E. E. Havinga and A. J. Bosman, Phys. Rev. 140, A292 (1965).

[10] All notation is that of J. F. Nye, in *Physical Properties of Crystals* (Oxford U. P., Oxford, England, 1960).

[11] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, (Pergamon, New York, 1960), p. 391; see also *Statistical Physics* (Pergamon, New York, 1969).

[12] G. B. Benedek and K. Fritsch, Phys. Rev. **149**, 647 (1966).

[13] G. E. Durand and A. S. Pine, IEEE J. Quantum Electron. **4**, 523 (1968).

[14] Assuming a conical arrangement which yields the largest angle of acceptance (but averages over anisotropy effects), angular resolution $\Delta\theta/\theta = 1/4$, and a scattering angle $\theta = 10$ mrad. A small scattering angle is required due to the long second-sound wavelength (cf. Refs. 3).

[15] A. Griffin, Rev. Mod. Phys. **40**, 167 (1968), and references cited there.

[16] R. K. Wehner and R. Klein, Physica 62, 161 (1972).

[17] J. Vallin, K. Markbund, J. O. Sikström, and O. Beckman, Ark. Fys. **32**, 515 (1966).

[18] R. J. Hardy and Jaswal, Phys. Rev. B **3**, 4385 (1971).

[19] Landolt-Börnstein, *Zahlenwerte und Funktionen*, 6th ed. (Springer-Verlag, Berlin, 1961), Vol. II, Pt. 4.

[20] D. Petrac and M. E. Woolf, Phys. Rev. Lett. **28**, 283 (1972).