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Pockels coefficients for rare-gas crystals

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New Brillouin scattering measurements with Xe single crystals lead to ratios of the Pockels elasto-optic coefficients ($p_{12}/p_{11} = 1.02 \pm 0.05$ and $p_{44}/p_{11} = 0.13 \pm 0.01$), which are consistent with the ratios for Kr and Ar crystals. The experimental values of the Pockels ratios for Xe, Kr, and Ar are used together with results from a recent theory of Brillouin scattering by Sipe, to obtain values of the Pockels coefficients and short-range-interaction parameters for these rare-gas crystals.

I. INTRODUCTION

A systematic study of the Brillouin spectra of crystalline Xe, Kr, Ar, and Ne has been carried out in this laboratory.[1] From measurements of Brillouin frequency shifts it has been possible to obtain precise values of the elastic constants[1,2] for these solids at their triple points. From measurements of relative intensities of Brillouin components, ratios of the Pockels elasto-optic coefficients p_{12}/p_{11} and p_{44}/p_{11} have been determined for Kr (Ref. 3) and Ar (Ref. 4); and absolute intensity measurements have given values of p_{11}, p_{12}, and p_{44} for Kr.[5] However, for Xe and Ne, only estimates of these ratios were possible because of the limited experimental data. For Xe,[6] the ratios ($p_{12}/p_{11} = 1.45$ and $p_{44}/p_{11} = -0.10$) differ from the respective ratios in Kr (1.00 ± 0.08 and 0.11 ± 0.01) and in Ar (0.98 ± 0.15 and 0.12 ± 0.05). For Ne,[7] a range of values is possible: at one extreme these ratios (0.85 and 0.11) compare well with those of Ar and Kr, at the other (1.35 and −0.10) with those of Xe. Finally, difficulties are encountered when comparing these experimental values with results of the available theory. For example, none of the experimental values appears to agree with a theory by Werthamer[8] based on a point dipole model of neutral and polarizable atoms, neglecting short-range interactions. Improved agreement is obtained with a theory by Oxtoby and Chandrasekharan[9] which includes short-range overlap and exchange effects. Numerical results, however, require a knowledge of the trace and anisotropy of the polarizability of interacting atomic pairs, and such data are presently available for Ne and Ar, but not for Kr and Xe.

Recently, a new set of experiments[2] with Xe single crystals has been carried out resulting in more accurate intensity measurements and new elasto-optic ratios which are in agreement with those of Ar and Kr. Also, a new theoretical treatment of Brillouin scattering from rare gas crystals has been developed by Sipe,[10] which includes short-range interactions, and local field corrections. His theory and the experimental ratios p_{12}/p_{11} and p_{44}/p_{11} have been used to evaluate the individual Pockels coefficients and short-range parameters for Xe, Kr, and Ar, and the results are presented here.

II. THEORETICAL REVIEW

Brillouin spectra of cubic crystals consist of three Lorentzian doublets, one for each of the three polarizations of sound waves ($\mu = a, b, c$). Each doublet occurs at frequency shifts $\pm\omega_\mu(\vec{q})$ corresponding to the sound mode frequencies. Ther relative intensities $I_a : I_b : I_c$ are given by $(F_a/\omega_a)^2 : (F_b/\omega_b)^2 : (F_c/\omega_c)^2$ where $F_{a,b,c}$ are known functions[1] of the elasto-optic coefficients p_{11}, p_{12}, p_{44}. Therefore, measurements of the relative intensities of the Brillouin components can be used to obtain ratios of the elasto-optic coefficients, and this has been done for the rare-gas crystals.

In Sipe's theory[10] of the Pockels elasto-optic coefficients, the atoms are regarded as polarizable particles coupled by the dipole-dipole interaction. Contributions of short-range interactions are included by considering an effective value $\bar{\alpha}$ of the atomic polarizability (α_0) that depends on the distance between an atom and its nearest neighbor in the rigid lattice. Sipe derives weighted elasto-optic constants $p'_{ij} = (4\pi\bar{\alpha}\bar{\rho}c_0)^{-1}p_{ij}$:

$$\begin{aligned} p'_{11} &= 1 - 2\bar{\alpha}\bar{\rho}c_1 - (\bar{\alpha}/\alpha_0)[12f_2(a) + 2af'_2(a) + 4af'_0(a)], \\ p'_{12} &= 1 + \bar{\alpha}\bar{\rho}c_1 - (\bar{\alpha}/\alpha_0)[-6f_2(a) - af'_2(a) + 4af'_0(a)], \\ p'_{44} &= \bar{\alpha}\bar{\rho}c_1 - (\bar{\alpha}/\alpha_0)[6f_2(a) + 3af'_2(a)]. \end{aligned} \tag{1}$$

Here $\bar{\rho}$ is the density in the absence of lattice strains, and $f_0(a)$, $f_2(a)$, and $f'_0(a)$, $f'_2(a)$ are short-range interaction parameters and their derivatives with respect to distance evaluated at the nearest-neighbor distance a. The parameter c_0 contains the local field correction and has the value $c_0 = (1 + 8\pi/3\bar{\rho}\bar{\alpha})^{-2}$; c_1 is a lattice sum, equal to

1.280 for face-centred-cubic crystals. When the short-range interactions are neglected, Eqs. (1) reduce to those derived by Werthamer,[8] but with a change of sign for all three terms in $\bar{\alpha}\bar{\rho}c_1$. They also result in the relation

$$1-p_{12}/p_{11}+3p_{44}/p_{11}=0 \tag{2}$$

given by Werthamer.

From Eqs. (1), it can be shown that

$$p'_{11}+2p'_{12}=[3-12(\bar{\alpha}/\alpha_0)af'_0(a)], \tag{3}$$

leading to the following relations for the weighted elasto-optic coefficients,

$$\begin{aligned} p'_{11}&=[3-12(\bar{\alpha}/\alpha_0)af'_0(a)](1+2p_{12}/p_{11})^{-1}, \\ p'_{12}&=p'_{11}p_{12}/p_{11}, \\ p'_{44}&=p'_{11}p_{44}/p_{11}. \end{aligned} \tag{4}$$

The importance of Eqs. (4) is that they provide a means of evaluating the individual coefficients once the ratios p_{12}/p_{11} and p_{44}/p_{11} and the value of $f'_0(a)$ are known. Expressions for the other short-range interaction parameters can be deduced from Eq. (3.36) of Sipe's paper[10] and from Eqs. (1), giving

$$\begin{aligned} f_0(a)&=(\bar{\alpha}-\alpha_0)(12\alpha_0)^{-1}, \\ f_2(a)&=(-p'_{11}+p'_{12}+p'_{44}-4\bar{\alpha}\bar{\rho}c_1)\alpha_0(12\bar{\alpha})^{-1}, \\ af'_2(a)&=(p'_{11}-p'_{12}-3p'_{44}+6\bar{\alpha}\bar{\rho}c_1)\alpha_0(6\bar{\alpha})^{-1}. \end{aligned} \tag{5}$$

The relations given in Eqs. (4) and (5) provide a quantitative link between measured intensity ratios of Brillouin components and microscopic polarizability properties of rare-gas atoms.

III. EXPERIMENT WITH Xe CRYSTALS

The experimental apparatus and method have been described in considerable detail elsewhere.[1,2] Four strain-free single crystals of Xe were grown and maintained at 160.5 K, and investigated in the usual way. Brillouin spectra were recorded for several orientations of each crystal (Fig. 1). Almost all of the spectra exhibited the longitudinal component (*L*) and one of the transverse components (T_1), but only rarely T_2 because of its low intensity. The frequency shifts and integrated intensities of the Brillouin components were measured and analyzed, and values of the elastic constants and elasto-optic ratios determined. The results of the elastic constant analysis confirmed the earlier values of Gornall and Stoicheff,[6] and have already been published.[2] Here, the discussion is limited to the evaluation of the elasto-optic coefficients and comparison with theory.

IV. RESULTS AND DISCUSSION

A. Elasto-optical ratios for Xe

Table I gives relative integrated intensities $I(T_1)/I(L)$ and $I(T_2)/I(L)$ measured for various orientations of the four Xe crystals. From the combined data for all four crystals, the elasto-optic ratios were found to be

$$p_{12}/p_{11}=1.02\pm0.05\ ,$$

$$p_{44}/p_{11}=0.13\pm0.01\ .$$

The quoted uncertainties include contributions from the statistical fit of the data and from errors in the elastic constants. Figure 2 shows the plot of the experimental intensity ratios vs crystal orientation, along with the calculated values based on the above elasto-optics ratios, for two of the crystals. There is good overall agreement.

These new values of p_{12}/p_{11} and p_{44}/p_{11} for Xe differ from the earlier estimates ($p_{12}/p_{11}=1.45$ and $p_{44}/p_{11}=-0.10$) reported by Gornall and Stoicheff,[6] but are in agreement, both in magnitude

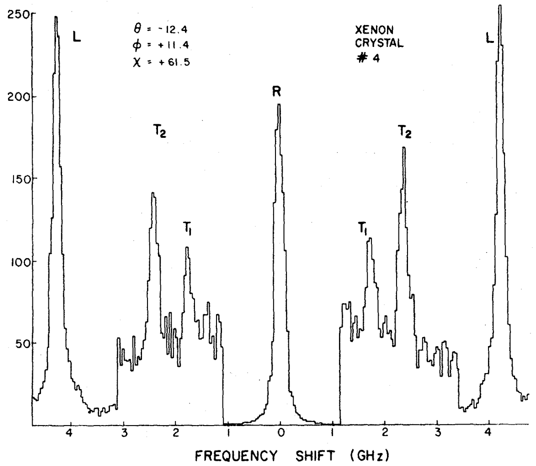

FIG. 1. Brillouin spectrum of a Xe single crystal at a temperature of 160.5 K.

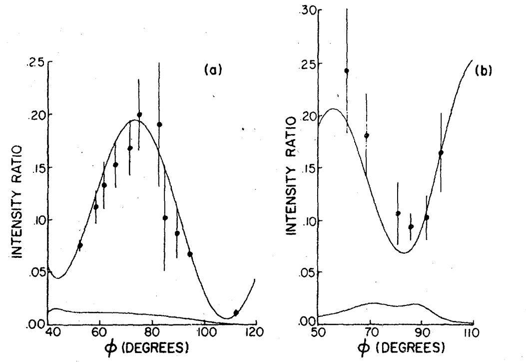

FIG. 2. Intensity ratios of the Brillouin components in the spectra of (a) crystal No. 1, and (b) crystal No. 2. The points with error bars are experimental ratios of $I(T_1)/I(L)$, and the solid lines are calculated values of $I(T_1)/I(L)$ and $I(T_2)/I(L)$ based on the Pockels coefficient ratios determined here.

TABLE I. Measured Brillouin intensity ratios for four Xe crystals at $T = 160.5$ K.

	Crystal orientation			Relative intensities	
Crystal no.	θ	ϕ	χ	$I(T_1)/I(L)$	$I(T_2)/I(L)$
1	−46.9	52.3	147.3	0.076 ± 0.005	···
	−46.9	58.4	147.5	0.113 ± 0.014	···
	−46.3	61.5	148.0	0.140 ± 0.016	···
	−46.9	65.9	147.8	0.156 ± 0.019	···
	−46.6	71.4	147.5	0.168 ± 0.012	···
	−45.3	74.9	148.0	0.192 ± 0.026	···
	−49.2	82.6	147.1	0.210 ± 0.039	···
	−49.4	84.9	147.0	0.127 ± 0.025	···
	−47.7	89.6	147.5	0.095 ± 0.015	···
	−47.0	94.5	147.5	0.067 ± 0.003	···
	−46.5	112.4	147.1	0.012 ± 0.002	···
2	−85.1	60.9	123.7	0.260 ± 0.042	···
	−79.6	68.7	126.0	0.165 ± 0.024	···
	−81.4	80.9	125.3	0.106 ± 0.030	···
	−80.9	85.9	125.4	0.095 ± 0.011	···
	−80.4	92.0	125.3	0.113 ± 0.011	···
	−83.1	97.5	125.4	0.149 ± 0.021	···
3	−79.5	−120.8	−55.8	0.195 ± 0.027	···
	−78.9	−96.0	−57.0	0.211 ± 0.025	···
	−79.3	−86.2	−57.0	0.168 ± 0.047	···
	−77.2	−76.6	−57.2	0.102 ± 0.026	···
	−75.5	−67.4	−57.8	0.114 ± 0.032	···
4	−12.2	5.4	57.8	0.029 ± 0.003	0.091 ± 0.010
	−12.4	12.4	61.5	0.042 ± 0.009	0.097 ± 0.012

and sign, with the ratios found for Ar and Kr. A reanalysis of the earlier data shows that the observed intensity ratios are compatible with the new ratios of the elasto-optic constants determined here. (The limited range of crystal orientations and the low intensities of the transverse components in the earlier study, precluded the determination of unique and accurate values for the elasto-optic ratios from that data alone.)

B. Pockels coefficients and short-range interaction constants for the rare-gas crystals

The available experimental values of the Pockels coefficients and ratios for the rare gas crystals are collected in Table II. It is seen that, within experimental error, the ratios p_{12}/p_{11} for Xe, Kr, and Ar are the same, namely 1.00; similarly the ratios p_{44}/p_{11} are the same; 0.12, almost one-tenth of p_{12}/p_{11}. Thus, it is tempting to accept these values for Ne as well, or at least the values $p_{12}/p_{11} = 0.85$ and $p_{44}/p_{11} = 0.11$, which were found to be compatible with the observed intensity ratios of the Brillouin components in Ne.

Table III lists the theoretical values of the Pockels coefficients and their ratios, calculated using Sipe's theory, Eqs. (1), but neglecting the short-range interactions. The values of the coefficients p_{11}, p_{12}, and p_{44}, as well as their ratios are found to increase slightly with increasing mass of the rare gas atoms. Also, the magnitudes of the theoretical values are consistent with the present experimental values, despite the neglect of short-range interactions.

This qualitative agreement between theory and experiment is very satisfying, and is an indication of the improvement in theoretical understanding of this problem. Further evidence comes from the fact that it is now possible to obtain information about the short-range interactions using Sipe's theory. First, it should be emphasized that the short-range (higher multipole and Van der Waals) interactions are not negligible in the rare-gas crystals at their triple points. This is immediately evident in forming the sum in Eq. (2). For Xe, Kr, and Ar, the respective sums (from the experimental values in Table II) instead of being zero are 0.37 ± 0.08, 0.33 ± 0.11, and 0.38 ± 0.31. This failure of the relation represented by Eq. (2), indicates that short-range interactions contribute significantly to Brillouin scattering intensities in the rare-gas crystals. Therefore, an analysis of the experimental data (Table II) taking into account short-range interactions is war-

TABLE II. Experimental values of Pockels coefficients and their ratios.

Atom	Xe[a]	Kr[b]	Ar[c]	Ne[d]
ρ (cm cm^{-3})	3.406 ±0.003	2.794 ±0.003	1.629 ±0.001	1.437±0.002
T (K)	160.5	115.6	82.3	24.3
λ (Å)	5145	4880	4880	4880
n	1.4536±0.0004	1.3487±0.0002	1.2708±0.0002	1.107±0.003
p_{12}/p_{11}	1.02 ±0.05	1.00 ±0.08	0.98 ±0.16	(0.85)[e]
p_{44}/p_{11}	0.13 ±0.01	0.11 ±0.01	0.12 ±0.05	(0.11)[e]
p_{11}	···	0.34 ±0.04	···	···
p_{12}	···	0.34 ±0.05	···	···
p_{44}	···	0.037 ±0.005	···	···

[a] Reference 6 and present experiment.

[b] References 3 and 5.

[c] Reference 4.

[d] Reference 7.

[e] Unique values cannot be deduced from the available data.

ranted.

At the outset, it should be emphasized that this is only possible for Kr. As seen in Table II, only for Kr are values of p_{11}, p_{12}, and p_{44} available for use with Eqs. (3) and (5) to determine all four parameters $f_0(a)$, $f_2(a)$, $af_0'(a)$, $af_2'(a)$. For Ar and Xe, only the ratios p_{12}/p_{11} and p_{44}/p_{11} are known, so that additional data or assumed values are required. Moreover, because the values of the short-range interaction parameters are expected to be small and because of the limited accuracy of the experimental Pockels coefficients for Kr, the derived values of the parameters should be considered as estimates only. A set of values for Kr is given in Table IV, calculated from Eqs. (3) and (5) and using the p_{ij}'s listed in Table II. If the value $f_0'(a) = -0.005$ Å^{-1} found for Kr is also assumed for Ar and Xe, then values for the individual Pockels coefficients can be calculated from Eqs. (4), and for the short-range interaction parameters from Eqs. (5). These values are also listed in Table IV.

Another set of p_{ij} values for each of Ar, Kr, and Xe was generated by assuming the value $f_0'(a) \equiv 0$. This parameter is the derivative of the trace of the pair polarizability with distance evaluated at the nearest-neighbor distance a. As justification for adopting the value $f_0'(a) \equiv 0$, it may be mentioned that graphs of the trace of the pair polarizability for both He and Ar, given by Oxtoby and Gelbart,[11] show slopes of almost zero at the nearest-neighbor distance. This assumption leads to the p_{ij}'s given in brackets in Table IV. A comparison of the two sets of values for each of Ar, Xe, and Kr, shows agreement to within ±10%. In particular, with $f_0'(a) \equiv 0$, the values for Kr agree to within experimental error with the values determined by Kato and Stoicheff.[3] This good agreement found for Kr may be taken as an indication that the value of $f_0'(a)$ is small and that its contribution to the Pockels coefficients amounts to only a few percent. On this basis, the recommended values for the Pockels coefficients of Ar are $p_{11} = 0.31 \pm 0.03$, $p_{12} = 0.30 \pm 0.03$, $p_{44} = 0.037 \pm 0.005$, and of Xe, $p_{11} = 0.36 \pm 0.03$, $p_{12} = 0.37 \pm 0.03$, $p_{44} = 0.047 \pm 0.005$.

TABLE III. Theoretical values of Pockels coefficients and their ratios, calculated[a] according to Sipe's theory without short-range interactions.

Atom	Xe	Kr	Ar	Ne
p_{11}	0.284	0.274	0.256	0.157
p_{12}	0.370	0.336	0.302	0.168
p_{44}	0.029	0.021	0.015	0.004
p_{12}/p_{11}	1.30	1.23	1.18	1.07
p_{44}/p_{11}	0.10	0.08	0.06	0.02

[a] Calculations were made for the experimental conditions given in Table II.

A comparison of the Pockels coefficients in Tables III and IV shows contributions of ~+20% in p_{11} and ~+40% in p_{44} for all three solids when the short-range interactions are included in the analysis according to Sipe's theory. The values for the short-range functions $f_0(a)$ and $f_2(a)$ appear to be essentially the same for Ar, Kr, and Xe (namely, -1×10^{-3} and -1×10^{-2}, respectively) despite large differences in a, α_0, and $\overline{\alpha}$ for the three solids. While in principle these values could be used to estimate the isotropic and anisotropic components of the pair polarizability for two atoms at a separation a, their limited accuracy does not justify such an evaluation at this time.

In summary, new experimental values for ratios of the Pockels coefficients have been obtained for Xe crystals at the triple point. From these values and those of Ar and Kr crystals, it is shown that short-range interactions are impor-

TABLE IV. Values of Pockels coefficients and short-range interaction parameters derived from experimental values of p_{12}/p_{11} and p_{44}/p_{11} (Table II) using Sipe's theory (Ref. 10).

Atom	Xe	Kr	Ar	Ne
α_0(Å^3) [a]	4.200	2.565	1.680	0.3992
$\bar{\alpha}$(Å^3) [b]	4.135	2.550	1.654	0.389
a (Å)	4.484 [c]	4.016 [d]	3.863 [e]	3.208 [f]
p_{11}	0.366 ± 0.015 (0.337)	0.340 ± 0.020 (0.315)	0.310 ± 0.035 (0.288)	
p_{12}	0.374 ± 0.030 (0.344)	0.340 ± 0.040 (0.315)	0.304 ± 0.080 (0.282)	
p_{44}	0.047 ± 0.005 (0.044)	0.037 ± 0.005 (0.035)	0.037 ± 0.020 (0.035)	
$f_0(a)\,(10^{-3})$	-1.3 ± 0.2	-0.5 ± 0.2	-1.3 ± 0.3	
$f_2(a)\,(10^{-2})$	-1.4 ± 0.2	-1.2 ± 0.3	-0.9 ± 0.6	
$af_0'(a)\,(10^{-2})$	-2.0	-2.0	-2.0	
$af_2'(a)\,(10^{-2})$	0.9	0.7	-0.9	

[a] Calculated from refractive indices of gases (Ref. 12) using the Lorentz-Lorenz relation $(n^2-1)/(n^2+2) = 4/3\pi\bar{\rho}\alpha_0$ for a fluid.

[b] Calculated from refractive indices of solids (Table II) using the Lorentz-Lorenz relation $(n^2-1)/(n^2+2) = 4/3\pi\bar{\rho}\bar{\alpha}$.

[c] Reference 13.

[d] Reference 14.

[e] Reference 15.

[f] Reference 16.

tant in the rare gas solids. A recent theory by Sipe is used to calculate the contributions of such interactions to the Pockels coefficients, amounting to 20% in p_{11} and 40% in p_{44}. Finally, values for the individual Pockels coefficients of Ar and Xe are derived from experimental ratios, using Sipe's theory, along with estimates of short-range interaction parameters for Ar, Kr, and Xe.

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