An idealized nonequilibrium mechanism in KCl:OH has in fact been studied[4]; namely, the formation of parallel dipole pairs which become nonalignable because their correlation energy is greater than the mean available phonon energy. The classical polarizability relation was used in this study, and good agreement with experimental data was obtained using a scale factor $\mu_e = 4.4$ Debye unit. These data were restudied using the $\rho \to \infty$ polarizability data of Fig. 1, and the curve-fitting μ_e was reduced to 4.0 Debye unit.

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[7] Ref. 1; see also M. E. Baur and W. R. Salzman, Phys. Rev. Letters 17, 159 (1966). The level scheme shown in Fig. 1 is valid only if 180° tunneling is neglected. If this tunneling is taken into account, the T_{1u} level can be above the E_g level.

[8] An electric field along, say, [100] will remove the degeneracy of the energy-level diagram (Ref. 6) and alter the polarizability, Eq. (2). The right-hand side of Eq. (1) is defined for zero applied field, but the dipole interactions will establish a local field in the sense that $\langle \vec{E}\vec{\mu} \rangle$ is nonzero, although $\langle E_{100} \rangle$ must necessarily vanish. Consequently, the dipole-interactions local field does not remove the degeneracy or affect Eq. (2), but rather adds a scale factor to the energy.

[9] For ρ values less than unity, $3kT\alpha(T)/\mu^2$ is greater than 1.0 on this temperature range. Since these values have the effect of increasing rather than limiting ϵ, they are not considered here.

[10] Baur and Salzman (Ref. 1) determined μ_1, μ_2, $\Delta_1(=2\Delta)$, and $\Delta_2(=3\Delta)$ by applying Eq. (1) and a form of Eq. (2) to dielectric data on KCl:OH, but neglecting interaction effects. They found that $\rho = (\mu_2/\mu_1)^2 \simeq 21$ and $\Delta/k \simeq 0.1$°K.

[11] W. Känzig, H. R. Hart, and S. Roberts, Phys. Rev. Letters 13, 543 (1964).

[12] The value $N = 28.6 \times 10^{18}$ cm^{-3} is the "dielectric concentration" determined from the linear plot of Eq. (1); chemical analysis of this crystal indicated $N = 36 \times 10^{18}$ cm^{-3}.

[13] H. Hart and S. Roberts, to be published, have in fact observed a remanent polarization in KCl:OH that decays in time; these measurements were made below the temperature of the maximum dielectric constant.

ELECTRIC-FIELD-INDUCED INFRARED ABSORPTION IN DIAMOND*

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In the presence of an external electric field, certain Raman-active vibration modes in diamond-type crystals also become infrared active, giving rise to an absorption proportional to the first-order change in the electronic polarizability per unit cell with the relative displacement of atoms, $\partial\alpha/\partial u$. We have observed such a transmission minimum and from its characteristics we have determined the electric-field-induced effective ionic charge and $\partial\alpha/\partial u$.

In crystals having the diamond structure, the effective ionic charge of the atoms is zero, and there is no first-order (one-phonon) resonance absorption of electromagnetic (em) radiation by the fundamental ($q \approx 0$) optical vibration modes. Such crystals do exhibit well-defined, although weak, absorption bands due to higher order electric-moment effects.[1] As shown by Burstein and Ganesan[2] and by Szigeti,[3] an externally applied static electric field, $\vec{E}(0)$, induces an "effective" ionic charge on the atoms, so that the $q \approx 0$ transverse optical (TO) and longitudinal optical (LO) vibration modes which are Raman active also become infrared active. The strength of absorption is proportional to the first-order change in the electronic polarizability per unit cell with the relative displacement of atoms, $\partial\alpha/\partial u$, which determines the corresponding intensity of the first-order Raman scattering. We report here our experimental observation at room temperature of an electric field-induced absorption band at 1336 cm^{-1} in diamond at an applied field of 1.2×10^5 V/cm. From the strength of the induced absorption band, we derive a value of 4×10^{-16} cm^2 for $\partial\alpha/\partial u$. This represents the first quantitative determination of $\partial\alpha/\partial u$ for diamond. From this value for $\partial\alpha/\partial u$ we obtain 3×10^{-7} for the Raman scattering efficiency per unit length of crystal per unit solid angle at 15 800 cm^{-1}, the frequency of the He-Ne laser line.

The effect, which is essentially the same as that predicted by Condon[4] for homonuclear molecules, and observed experimentally by Crawford and Dagg[5,6] for H_2 molecules at fields of 10^5 V/cm, may be visualized as follows: An applied electric field induces a dipole moment in each primitive unit cell. The relative displacement of the atoms in the $q\approx0$ optical vibration modes produces a change in the electronic polarizability of the atoms and, consequently, the induced dipole moment varies in amplitude and orientation at the frequency of the modes. The induced "effective" ionic charge is given by $e^*=\partial M/\partial u=(\partial\alpha/\partial u)E(0)$ where M is the electric moment per primitive unit cell and u is the relative displacement of the atoms in the unit cell. A measurement of strength of the absorption band, which is proportional to $e^{*2}=|(\partial\alpha/\partial u)E(0)|^2$, can, therefore, provide quantitative information about the first-order Raman matrix elements.

The electronic polarizability can be expanded in powers of the relative displacements of the atoms as follows:

$$\alpha=\alpha^{(0)}+\sum_{j,q}\frac{\partial\alpha}{\partial u(j,q)}\delta u(j,q)+\cdots$$
$$=\alpha^{(0)}+\alpha^{(1)}+\cdots, \qquad (1)$$

where the index j indicates the optical branch and $\vec{q}$ is the wave vector of the particular mode of vibration. When a static electric field $\vec{E}(0)$ is applied, the dipole moment induced per unit cell is given by

$$\vec{M}=\alpha\cdot\vec{E}(0)=\alpha^{(0)}\cdot\vec{E}(0)+\alpha^{(1)}\cdot\vec{E}(0)+\cdots$$
$$=\vec{M}^{(0)}+\vec{M}^{(1)}+\cdots, \qquad (2)$$

where α by definition includes any local field effects. Since there is no contribution from lattice vibrations to the polarizability, the static and optical-frequency values are essentially the same, i.e., $\alpha(0)\approx\alpha(\omega)$. The first term of Eq. (2) represents the static electric moment. The second term represents the time-varying electric moment which provides the coupling to the infrared radiation. The μth component of $\vec{M}^{(1)}$ can be expressed in full tensor notation as

$$M_\mu^{(1)}=\alpha_{\mu\lambda}^{(1)}E_\lambda(0)$$
$$=\sum_{j,q}\left(\frac{\partial\alpha}{\partial u(j,q)}\right)_{\mu\lambda,\sigma}E_\lambda(0)\delta u_\sigma(j,q)$$
$$\equiv\sum_{j,q}e_{\mu\sigma}{}^*(j,q)\delta u_\sigma(j,q), \qquad (3)$$

where μ,λ,σ designate components along X_1, X_2, and X_3, the crystallographic axes, and summation over any repeated index is implied. Here

$$e_{\mu\sigma}{}^*(j,q)=\left(\frac{\partial\alpha}{\partial u(j,q)}\right)_{\mu\lambda,\sigma}E_\lambda(0)\equiv\alpha_{\mu\lambda,\sigma}E_\lambda(0) \qquad (4)$$

is a second-rank tensor which represents the electric-field-induced charge of the atoms, associated with the particular mode of vibration (j,q). We neglect, for present purposes, the effect of the electric field on $\partial\alpha/\partial u$ and on the amplitude of vibration, since these effects are proportional to $E(0)^2$ and only affect the intensity of the absorption to terms of order higher than $E(0)^2$.

The selection rule for the absorption of em radiation by a given optical vibration mode is that $\vec{M}\cdot\vec{E}(\omega)\neq0$ where $\vec{E}(\omega)$ is the electric field of the em radiation. Thus, absorption can take place, provided the time-varying electric moment $\vec{M}^{(1)}=\alpha^{(1)}\cdot\vec{E}(0)$ has a component along $\vec{E}(\omega)$, i.e., provided

$$\vec{E}(\omega)\cdot\alpha^{(1)}\cdot\vec{E}(0)\neq0$$

or

$$\mathcal{E}_\mu(\omega)\alpha_{\mu\lambda,\sigma}(j,q)d_\sigma(j,q)\mathcal{E}_\lambda(0)\neq0, \qquad (5)$$

where $\vec{\mathcal{E}}(\omega)$, $\vec{\mathcal{E}}(0)$, and $\hat{d}(j,q)$ are the unit polarization vectors for the em radiation, static electric field, and (j,q)th phonon, respectively. In addition, one has the usual requirement of energy and momentum conservation for first-order (one-phonon) processes, $\Delta n=\pm1$, $\hbar\omega(j,q)=\hbar\omega(\vec{k})$, and $\vec{q}_j=\vec{k}\approx0$. For the triply degenerate $q\approx0$ optical vibration modes of the diamond structure, the tensor $\alpha_{\mu\lambda,\sigma}$ in Eq. (5) is equal to $|e_{\mu\lambda\sigma}|a$ where a is the single independent component of the tensor, and $e_{\mu\lambda\sigma}$ is the Levi-Civita function.[7-9] Thus, absorption of em radiation will take place when there are components of $\vec{E}(\omega)$, $\vec{E}(0)$, and $\vec{u}(j,0)$ along the crystallographic axes, which are mutually orthogonal.

The selection rule for the electric field absorption of em radiation is the same as that for first-order Raman scattering if one replaces $E(0)$ by $E(\omega_S)$, the electric field of the scattered radiation. Correspondingly the $(q \approx 0)$ LO as well as the $(q \approx 0)$ TO vibration modes can absorb em radiation in the presence of an external electric field.

The contribution of the electric-field-induced (one-phonon) absorption processes to the frequency-dependent dielectric constant is given by[10,11]

$$\epsilon_{\mu\nu}{}^{(1)}(\omega) = \frac{4\pi N}{\bar{m}} \sum_j \frac{M_\mu{}^{(1)}(j,0) M_\nu{}^{(1)}(j,0)}{\omega(j,0,E)^2 - \omega^2 - i\omega\gamma(j,0,E)},$$

$$M_\mu{}^{(1)}(j,0) = e_{\mu\sigma}{}^{*}(j,0) d_\sigma(j,0), \qquad (6)$$

where $\bar{m} = m/2$ is the reduced mass of the two atoms in the unit cell, and $\omega(j,0,E)$ and $\gamma(j,0,E)$ are the frequency and damping constants of the $(j, q \approx 0)$th optical vibration mode in the presence of an applied field.[12,13] For the diamond structure, which has a center of inversion, the variation of $\omega(j,0,E)$ and $\gamma(j,0,E)$ will be quadratic in $E(0)$. They are treated here as empirical parameters.

Attempts to observe an electric-field-induced absorption band in a diamond-type crystal were first carried out on silicon using samples with Li-diffused p-n junctions. The infrared beam was passed through the junction region, which was approximately 1 mm wide, in a direction parallel to the plane of the junction. No change in transmission was observed at the highest reverse-bias electric field ($\approx 10^4$ V/cm) that could be applied without excessive heating. The inability to observe an electric-field-induced absorption band is due in part to the low electric field used, and in part to the relatively high background absorption due to two-phonon absorption processes (≈ 2 cm^{-1}) in the vicinity of the frequency of the $q \approx 0$ optical vibration modes. We therefore turned our attention to diamond, in which higher field strengths are possible, and in which the background absorption due to two-phonon processes in the vicinity of 1332 cm^{-1}, the frequency of the $q \approx 0$ optical vibration modes, is relatively small (<0.2 cm^{-1} in type-IIa diamonds).

Transmission measurements were made at room temperature on a type-IIa diamond plate in the form of a rectangular parallelepiped having $(1\bar{1}0)$, (110), and (001) polished faces, kindly supplied by the Diamond Research Laboratory, Johannesburg, South Africa (Fig. 1). The crystal was mounted in a vacuum cell, and an electric field was applied between the (001) faces using evaporated gold films as electrodes. The highest field that we were able to apply, before arcing occurred at the crystal surfaces, was 1.2×10^5 V/cm. Unpolarized radiation from a Globar source was sent through the crystal along the $[1\bar{1}0]$ direction and the transmitted radiation was analyzed by a Perkin-Elmer grating spectrometer (model 12C) and thermocouple detector system operating at 13 cps and having an estimated resolution of 1 cm^{-1}. A PAR low-noise amplifier (model CR-4) and a PAR lock-in amplifier (model JB-4) were used to obtain optimum signal-to-noise ratios. In the absence of an applied electric field, there was no measurable absorption in the region of 1332 cm^{-1}. In the presence of a field of 1.2×10^5 V/cm a transmission minimum with $\Delta T/T = 2.5\%$ was observed at 1336 cm^{-1} with a signal-to-noise ratio of 4 to 1. The shift of 4 cm^{-1} from 1332 cm^{-1} is larger than the experimental error and is tentatively attributed to an electric-field-induced shift in frequency.[12,13]

For em radiation propagating in the $(1\bar{1}0)$ plane, the nonzero contributions to $\epsilon_{\mu\nu}{}^{(1)}(\omega)$ are those for which $\vec{\mathscr{E}}(\omega)$, $\vec{\mathscr{E}}(0)$, and $\vec{d}(j,0)$ are mutually orthogonal to one another due to the restriction $\mu \neq \lambda \neq 0$. Therefore, for the configuration used in this experiment with $\vec{E}(0)$ along [001] and $\vec{q}$ along $[1\bar{1}0]$, only the component

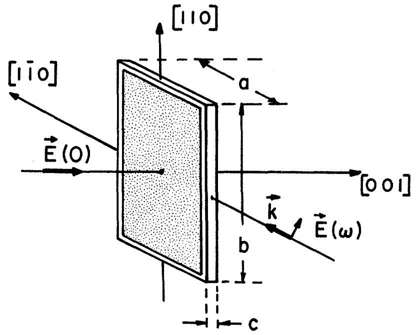

FIG. 1. Schematic diagram of the diamond plate used in the experiment, showing the directions of the applied field and of the infrared radiation. The dimensions of the plate are $a = 3.4$ mm, $b = 8.0$ mm, and $c = 0.50$ mm.

of the em radiation with $\vec{\mathcal{E}}(\omega)$ along [110] and the LO vibration mode with $\hat{d}(j,0)$ along $[1\bar{1}0]$ interact. Since only one polarization component of the em radiation is active, we multiply the observed $\Delta T/T$ by a factor of 2 in obtaining the absorption constant of the electric-field-induced band. On this basis we obtain $\Delta A = 9 \times 10^{-7} E(0)^2$ cm^{-1} with $E(0)$ expressed in cgs units. Assuming a band width of 1 cm^{-1} corresponding to $\gamma_L/\omega_L = 10^{-3}$, we obtain $e^*/e = 7\times 10^{-7} E(0)$, and $\partial\alpha/\partial u = 4\times 10^{-16}$ cm^2 per unit cell.

The Raman scattering efficiency per unit crystal length per unit solid angle for vibration modes with $\vec{q}$ vectors in the $[1\bar{1}0]$ direction can be calculated from $\partial\alpha/\partial u = a$ using the expression[9,14]

$$S = \frac{3\hbar\omega_s^{\,4} N^2}{\rho c^4 \omega_0} |a|^2 (n_0+1), \qquad (7)$$

where $\omega_s = \omega_i - \omega_0$; $\omega_0 = 1336$ cm^{-1}; $\omega_i = 15\,800$ cm^{-1}, the He-Ne laser excitation frequency; $n_0 + 1 \simeq 1$ at room temperature; N is the number of unit cells per unit volume; and ρ is the crystal density. We obtain a value of 3×10^{-7} for S in agreement with Loudon's theoretical estimate of 10^{-6} to 10^{-7} based on a deformation-potential calculation.[15]

Finally, we calculated a value of $\partial\alpha/\partial u = 3.8 \times 10^{-16}$ cm^2 for the Q branch ($\Delta J = 0$) vibration modes of molecular H_2, using Crawford and MacDonald's[6] data on the electric-field-induced infrared absorption. That molecular H_2 and diamond have essentially the same $\partial\alpha/\partial u$ values must, for the present, be considered as an interesting experimental fact.

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