RESEARCH NOTES

Temperature Dependence of the Dielectric Constant of Diamond

BY P. T. NARASIMHAN
Department of Physics, Indian Institute of Science, Bangalore 3

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Abstract. The temperature dependence of the dielectric constant of diamond has been measured over the temperature range 50–200°C. The value of $\epsilon^{-1}d\epsilon/dT$ over this range is $+1\times10^{-5}$. Details of the method of measuring the temperature coefficient of dielectric constant are also given. The magnitude and sign of $\epsilon^{-1}d\epsilon/dT$ for diamond has been theoretically calculated using Maxwell's relationship and Kramers–Heisenberg theory. The agreement between theoretical and experimental values is extremely good.

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§ 1. INTRODUCTION

IN the course of their extensive measurements on the dielectric constant of diamond, Whitehead and Hackett (1939) noticed that the value showed a slight increase with temperature at about 60°C. This increase was of the order of 1·5 to 2·5%, but with the limited accuracy of their apparatus they could only point out that the dielectric constant of diamond is substantially independent of temperature and thus in accordance with the Lorentz theory. The value of $5{\cdot}68\pm0{\cdot}03$ obtained by these authors is identical with the square of the refractive index for infinite wavelength, n_∞. Thus Maxwell's relationship $\epsilon=n_\infty^2$ (ϵ is the static dielectric constant) is very well obeyed (see also Frohlich 1949). Now, accurate determinations of the variation of the refractive index of diamond at optical frequencies (Ramachandran 1947) show that the value of dn/dT is appreciable and has a positive value at temperatures above −100°C. From the order of magnitude of the dn/dT values it is evident that the variation of the dielectric constant of diamond with temperature will probably be of the order of only 10^{-5}. Even in the case of ionic crystals the values of $\epsilon^{-1}d\epsilon/dT$ are known to be of the order of only 10^{-4} (Bretscher 1934, Eucken and Buchner 1935). The slight increase in the value of the dielectric constant observed by Whitehead and Hackett was explained by Hartshorn (see the discussion following the paper of Whitehead and Hackett 1939) as due to the increased conductivity of the liquid mixture used in their measurements. In fact with the apparatus of Whitehead and Hackett the true effect could not have been measured at all owing to the very small order of magnitude. In the present work we have been able to measure the value of $\epsilon^{-1}d\epsilon/dT$ of diamond in the temperature range 50–200°C by means of a heterodyne beat apparatus and have found that the value is indeed of the order of 10^{-5} and is positive.

Ramachandran (1947) has derived a quantitative expression for the value of dn/dT on the basis of Kramers–Heisenberg theory from a knowledge of the characteristic frequencies and strength of the harmonic oscillators (ν_{0k} and f_{0k} respectively). Since Maxwell's relation has been known to hold good in the case of diamond it is possible to calculate the temperature coefficient of the dielectric constant of diamond on lines similar to Ramachandran's. Remarkable agreement between the theory and experiment has been found, as will be seen presently.

§ 2. EXPERIMENTAL DETAILS AND THE VALUE OF $\epsilon^{-1}\, d\epsilon\ dT$

The changes in the dielectric constant were measured by changes in the capacity using the heterodyne beat apparatus which has been already described elsewhere (Narasimhan 1953). The voltage supply for the entire unit was taken from a constant voltage transformer. The frequency stability of the apparatus was remarkable (one beat per 10 seconds could be maintained for a period of several hours). For the measurement of the small capacity changes due to temperature an accurate variable air condenser of the stepped-rod type (Watson, Rao and Ramaswamy 1934) was used in parallel with the crystal condenser. This variable condenser had a total capacity of about 20 μF with a variable capacity of about 1·2 μF corresponding to about sixty revolutions of the graduated drum (360 divisions). A revolution counter attached to this drum made the readings easier. The condenser was calibrated as usual, before use. In the circuit was also a precision variable air condenser of the vane type which served the purpose of getting the heterodyne note within the coverage of the Watson condenser. After this adjustment, the precision condenser was kept ' locked '.

The diamond used in the present measurements was in the form of a nearly rectangular plate (length 6 mm, breadth 4 5 mm, thickness 1 1 mm, weight 69·4 mg). The two broader surfaces of this plate were aluminized fairly thickly so as to form the two plates of the crystal condenser. The crystal cell consisted of a brass container (3 in. in diameter, $\frac{5}{16}$ in. thick, $2\frac{1}{2}$ in. high) with a removable lid screwed on top. It was first silvered and then given a thick coating of gold in the interior. In the inside bottom of the cell was mounted a circular piece of ceramic insulator (2 in. in diameter, $\frac{1}{2}$ in. thick) on which was screwed a brass disc ($1\frac{1}{2}$ in. in diameter, $\frac{1}{8}$ in. thick) carrying a terminal for connecting the radio-frequency lead. This brass disc was also gold coated. The aluminized diamond plate was placed over this disc while a thick earthed metal probe contacted the other side of the diamond plate. The lead from the brass disc was taken out through a hole ($\frac{1}{2}$ in. in diameter) made at the side of the outer brass vessel Covering this hole was a ceramic insulator carrying a terminal to which was connected the lead from the brass disc. The crystal cell was connected to the heterodyne apparatus by a shielded lead, the brass vessel forming the earthed electrode. The crystal cell could be heated to desired temperatures by means of a wire resistance heater strip placed at the outside bottom of the cell.

Temperatures were measured both by a mercury thermometer and a thermocouple at various points of the cell. The difference in temperature between the inner brass disc and the outer vessel was less than 0 5°c and thus it was found convenient to measure temperatures from outside. Regulation at desired temperatures could be effected not only by varying the input current to the heater strips but also by use of a bi-metallic strip arrangement. It was found desirable to work above room temperature since at lower temperatures the effect of moisture made the readings unreliable. Thus the temperature range 50–200°c was found convenient and the capacity changes were also within the coverage of the Watson condenser. The measurements involved in the first instance the accurate determination of the capacity change due to the crystal cell itself, i.e. without the diamond plate. This was obtained by a series of measurements over the required temperature range, the values being consistently reproducible. Measurements were then carried out with the diamond plate in the cell whereby the capacity C of the diamond plate and its variation with temperature dC/dT were obtained. The average of a series of determinations gave the value of

$$\frac{1}{C}\frac{dC}{dT} = +1\cdot1 \pm 0\cdot1 \times 10^{-5}$$

over the temperature range 50–200°c. According to Eucken and Buchner (1934)

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \frac{1}{C}\frac{dC}{dT} - \alpha$$

where α is the coefficient of linear expansion of the crystal. The thermal expansion of diamond has been accurately determined by Krishnan (1946 a) over a wide temperature range. From Krishnan's data the value of α is seen to be only of the order of 1 to 2×10^{-6} over the present range, and since the uncertainty in the value of $C^{-1}dC/dT$ is also of this order we may omit this correction here. In our measurements, the variation with temperature of $\epsilon^{-1}d\epsilon/dT$, if any, could not be measured, chiefly due to the small size of the diamond.

§ 3. DISCUSSION

If we assume with Whitehead and Hackett that the Lorentz relationship holds good in diamond, that is,

$$\frac{\epsilon-1}{\epsilon+2}\frac{1}{\rho} = \text{constant} \qquad \ldots\ldots(1)$$

then the value of $\epsilon^{-1}d\epsilon/dT$ will be given by

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \frac{1}{\epsilon}\frac{\epsilon^2+\epsilon-2}{3}\frac{1}{\rho}\frac{\partial\rho}{\partial T}. \qquad \ldots\ldots(2)$$

Now, since $\rho^{-1}\partial\rho/\partial T = -\gamma$ where γ is the coefficient of cubic expansion, we have

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = -\frac{1}{\epsilon}\frac{(\epsilon^2+\epsilon-2)}{3}\gamma. \qquad \ldots\ldots(3)$$

Thus we should expect a diminution in the dielectric constant with increase of temperature. The observed positive value cannot therefore be explained as a pure density effect. On the other hand we can calculate the value of $\epsilon^{-1}d\epsilon/dT$ on lines similar to those used by Ramachandran (1947) for the calculation of dn/dT. We have according to Kramers–Heisenberg theory

$$n^2 = 1 + \sum_{\lambda} \frac{f_{0\lambda}}{\nu_{0\lambda}{}^2 - \nu^2}. \qquad \ldots\ldots(4)$$

Since Maxwell's relation holds good in diamond we also have

$$\epsilon = n_{\infty}{}^2. \qquad \ldots\ldots(5)$$

From this it follows that

$$\epsilon = 1 + \sum_{\lambda} \frac{f_{0\lambda}}{\nu_{0\lambda}{}^2}\,. \qquad \ldots\ldots(6)$$

Differentiating (6) with respect to T we get

$$\frac{d\epsilon}{dT} = \sum_{\lambda} \left\{ -\frac{2f_{0\lambda}}{\nu_{0\lambda}{}^3}\frac{d\nu_{0\lambda}}{dT} + \frac{1}{\nu_{0\lambda}{}^2}\frac{df_{0\lambda}}{dT} \right\}. \qquad \ldots\ldots(7)$$

Following Ramachandran it can be shown that

$$\frac{1}{\nu_{0\lambda}{}^2}\frac{df_{0\lambda}}{dT} = -\gamma(\epsilon - 1).$$

Introducing the quantity

$$\chi_{\lambda} = \frac{1}{\lambda_{0\lambda}}\frac{d\lambda_{0\lambda}}{dT} = -\frac{1}{\nu_{0\lambda}}\frac{d\nu_{0\lambda}}{dT}$$

we may write $\frac{d\nu_{0\lambda}}{dT} = -\chi_{\lambda}\nu_{0\lambda}$.

Finally we get

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \frac{1}{\epsilon}\left\{ -\gamma(\epsilon - 1) + 2\sum_{\lambda}\frac{f_{0\lambda}\chi_{\lambda}}{\nu_{0\lambda}{}^3} \right\} \qquad \ldots\ldots(8)$$

or

$$\frac{1}{\epsilon}\frac{d\epsilon}{dT} = \frac{1}{\epsilon}\left\{ -\gamma(\epsilon - 1) + 2\sum_{\lambda} f_{0\lambda}\lambda_{0\lambda}{}^2\chi_{\lambda} \right\}. \qquad \ldots\ldots(9)$$

For diamond, Peter (1923) has given the following values: $k=1$, 2; $f_{01} = 3{\cdot}859 \times 10^{10}$; $f_{02} = 1\ 080 \times 10^{9}$; $\lambda_{01} = 1060$ Å; $\lambda_{02} = 1750$ Å. Ramachandran has taken the value of $\chi_{\lambda} = \chi_1 = \chi_2$ and has shown it to correspond with the lattice frequency 1332 cm^{-1}. Taking Krishnan's (1946 b) value of $\chi = 9\ 6 \times 10^{-6}$ the calculated value of $\epsilon^{-1}d\epsilon/dT$ is found to be $+1{\cdot}25 \times 10^{-5}$ in very good agreement with the experimental value of $+1 \times 10^{-5}$.

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