(*Reprinted from Nature, Vol.* 169, *p.* 702, *April* 26, 1952)

Thermionic Constants of Graphite

SOME years ago, one of us (K. S. K.) suggested a new method of determining the thermionic constants of solids. The method is based on the determination of the saturation vapour pressure of the electron gas in equilibrium with the substance at different known temperatures. In practice, this is done by finding the rate of effusion into vacuum of electrons out of a small hole in a thin wall of a chamber scooped out of the substance. Using a well-known thermodynamic relation, analogous to the Clapeyron–Clausius equation connecting the temperature variation of the saturation vapour pressure of a given substance with its latent heat of evaporation, one obtains readily the thermionic constants. The work function of graphite was determined by this method by Dr. A. S. Bhatnagar[1], and of a few other substances by Dr. S. B. L. Mathur[2]; but the A coefficients in Richardson's equation were not determined by these authors, owing to uncertainties in some of the absolute measurements.

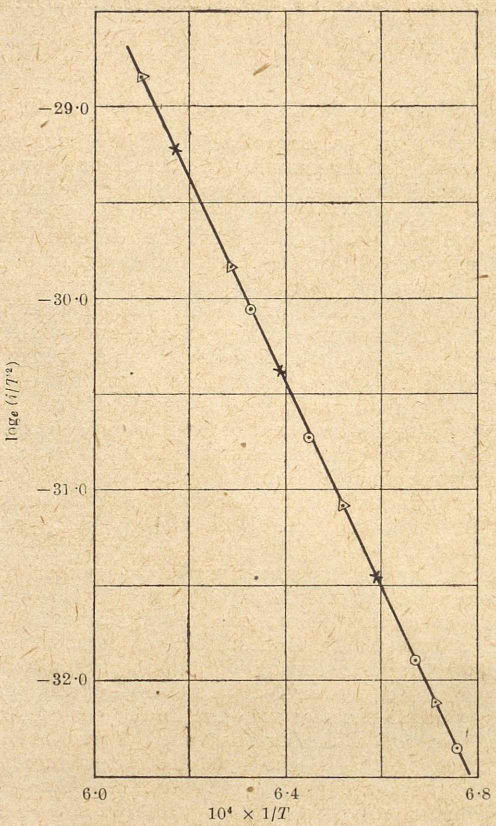
We have now improved the experimental technique, particularly to keep the temperature of the chamber uniform throughout, and the apparatus is now enclosed in a sealed glass vessel; this enables us to work in a better vacuum, and to ensure a mean free path of the electrons much larger than the dimensions of the apparatus. In order to eliminate the electrons emitted by the graphite surface adjoining the effusion hole, the surface is suitably covered by a thin mica sheet; a hole punctured in the sheet serves as the effective effusion hole. The area of the effusion hole is determined indirectly from the observed rate of loss of a suitably selected substance like naphthalene, or *p*-dichlorobenzene, kept inside the chamber, in vacuum, the loss being due to the sublimation of the substance and its subsequent effusion through the hole.

We reproduce in the graph the results obtained in three typical sets of measurements with graphite, in which $\log_e(i/T^2)$ is plotted against $1/T$, where i is the saturation current in amperes corresponding to effusion, per unit area of the effusion hole, in all directions, and T is the absolute temperature. The slope of the curve determines $-\varphi/k$, where k is the Boltzmann constant and φ is the work function, and it is found to correspond to:

$$\varphi = 4 \cdot 62 \pm 0 \cdot 02 \text{ eV.}$$

The intercept of the curve on the y-axis at $1/T = 0$ gives $\log_e A$, from which we find

$$A = 60 \pm 2 \text{ amp. cm.}^{-2} \text{ deg.}^{-2}.$$



This is almost exactly the value that one obtains for good metals.

This method of determining the thermionic constants has certain merits over the usual methods, in that it does not involve a knowledge of the effective area of the emitting surface, which is difficult to determine, or of the reflexion coefficient of the electrons at the surface of emission. Any localized stray impurities in the chamber, as, for example, small bits of copper or zinc deliberately introduced, are found to have no influence on the observation ; this is understandable, since the contact potential between the material of the walls of the chamber and the inserted metal will be almost exactly the difference between their work functions.

K. S. Krishnan
S. C. Jain

National Physical Laboratory of India,
New Delhi.

Nov. 14.

[1] *Proc. Nat. Acad. Sci., Ind.*, A, **14**, 5 (1944).

[2] Doctorate thesis, University of Allahabad ; see also *Proc. Ind. Sci. Cong. Assoc.* 1950, p. 23.

Printed in Great Britain by Fisher, Knight & Co., Ltd., St. Albans.

(*Reprinted from Nature, Vol.* 170, *p.* 159, *July* 26, 1952)

Polarization Field and the Acoustic Modes of Oscillation of Alkali Halide Crystals

In a recent paper[1], the frequency of the principal lattice oscillation of an alkali halide crystal, in which the lattice of the alkali ions oscillates with respect to the lattice of the halide ions, was calculated on the basis of the simple Born model. It was found that the electric polarization of the crystal that accompanies this oscillation leads to a polarization field of the Lorentz type which tends to increase the relative displacement of the two lattices and has thus a marked influence on the principal frequency. Microscopically, this polarization may be regarded as due to small dipoles located at the lattice points. Because of the small amplitude of the oscillation, these dipoles will be practically point-dipoles, and since they are also cubically arranged, the polarization field will have just the Lorentz value, namely, $4\pi/3$ times the polarization per unit volume. (Indeed, this appears to be the only case where the conditions postulated by Lorentz for obtaining the factor $4\pi/3$ are rigorously satisfied.)

The important part which the polarization field plays in determining the resonance frequency of the crystal is indeed to be expected from other considerations. Let us consider, for example, the dielectric constant of the crystal, and confine attention to the contribution from the relative displacements of the positive and the negative ions, as distinguished from the electronic polarizations of the ions themselves. Then the effect of the polarization field on the dielectric constant may be taken into account in two alternative ways. We may regard the effective field that produces the polarization as consisting of not only the 'field in the medium', but also the polarization field, in which case we obtain a formula of the Lorentz type :

$$\frac{K_\omega - 1}{K_\omega + 2} = \frac{C/3}{\Omega_i^2 - \omega^2}, \qquad (1)$$

in which Ω_i is *not* the resonance frequency of the crystal but a certain hypothetical frequency which the crystal would have, had there been no polarization field to affect it. Resonance will occur when the right-hand side of (1) tends to unity, that is, when

$$\omega^2 \rightarrow \omega_i^2 = \Omega_i^2 - C/3. \qquad (2)$$

Alternatively, we may regard the effect of the polarization field as confined wholly to changing the hypothetical frequency Ω_i to the actual resonance frequency ω_i of the crystal, in which case we obtain the Drude formula :

$$K_\omega - 1 = \frac{C}{\omega_i^2 - \omega^2}, \tag{3}$$

in which C has the same value as in (1).

The relation between the two frequencies ω_i and Ω_i may also be expressed in the form :

$$\Omega_i^2 = \omega_i^2 \left(\frac{K_0 + 2}{3}\right), \tag{4}$$

or more generally,

$$\Omega_i^2 - \omega^2 = (\omega_i^2 - \omega^2) \left(\frac{K_\omega + 2}{3}\right). \tag{5}$$

The acoustic modes of oscillation also lead to a finite polarization of the crystal, since the amplitudes of the two ions are in general different, as a result of the difference in their masses. Though the polarization now is much smaller than in the optical oscillations, the resulting polarization field is still comparable with the field due to the electrostatic and the repulsion interactions between the ions displaced by the acoustic wave.

We have studied the effect of this polarization field on the low-frequency acoustic oscillations in detail, and we find that the polarization field affects considerably the relative amplitudes of the two ions, but their frequencies remain completely unaffected by it (unlike the optical frequencies). This is very satisfactory, since otherwise the well-known Christoffel relations connecting the velocities of propagation of acoustic waves in the crystal with its elastic constants will be disturbed.

Note added in proof, June 30. Detailed investigations on the effect of the polarization field on the acoustic modes of oscillation have since been published (Krishnan and Roy, *Proc. Roy. Soc.*, A, 210, 481 (1951)).

K. S. Krishnan
S. K. Roy

National Physical Laboratory of India,
New Delhi.
Jan. 5.

[1] *Proc. Roy. Soc.*, A, 207, 447 (1951).

Printed in Great Britain by Fisher, Knight & Co., Ltd., St. Albans.

128

From the PHILOSOPHICAL MAGAZINE, Ser. 7, vol. xliii, p. 1000,
September 1952.

The Dispersion Formulae and the Polarization Fields

By SIR K. S. KRISHNAN, F.R.S., and S. K. ROY
The National Physical Laboratory of India, New Delhi

IN the usual derivation of the Drude formula for the dielectric constant of a dense medium as a function of the frequency of the incident waves, since one does not invoke the presence of a polarization field, and since further it is known that the Lorentz dispersion formula reduces to the Drude formula in the special case when the polarization field is made to vanish, any verification of the Drude dispersion formula is sometimes taken to imply the absence of a polarization field. This conclusion is not justified, and it is the main purpose of this note to emphasize that the Drude formula for the dielectric constant as a function of the frequency of the incident waves (as distinguished from the formula for the dielectric constant as a function of the density) is perfectly consistent with the occurrence of a polarization field having the Lorentz value, or any other value. This will be the case even when the polarization field factors

p_{ij} defining the polarization field acting on any oscillator of type i due to all the oscillators of type j in the medium differ from the Lorentz value $4\pi/3$, and differ from one another. In other words, irrespective of the actual polarization field that occurs in the medium, i.e. irrespective of the actual values of p_{ij} that define this field, the observational data for the dispersion of the dielectric constant can always be represented by the Drude formula

$$\epsilon_\omega - 1 = \sum_i \frac{A_i}{\omega_i^2 - \omega^2}, \quad \ldots\ldots\ldots \quad (1)$$

the characteristic frequencies ω_i that appear in the formula being the resonance frequencies of the medium.

The same observational data can also be fitted alternatively into a formula of the type

$$\epsilon_\omega - 1 = 4\pi\chi = 4\pi\sum_i \chi_i, \quad \ldots\ldots\ldots \quad (2)$$

where

$$\chi_i = \frac{B_i}{\Omega_i^2 - \omega^2}\left(1 + \sum_j p_{ij}\chi_j\right), \quad \ldots\ldots \quad (3)$$

in which j can take all values $i, j, k, \ldots.$ When all the p_{ij}'s have the same value, equal to p say, $\sum_j p_{ij}\chi_j = p\chi$, and eqn. (2) reduces to the form

$$\frac{\epsilon_\omega - 1}{\epsilon_\omega + \alpha} = \sum_i \frac{C_i}{\Omega_i^2 - \omega^2}, \quad \ldots\ldots\ldots \quad (4)$$

where

$$\alpha = \frac{4\pi}{p} - 1, \quad \ldots\ldots\ldots \quad (5)$$

and

$$C_i = pB_i. \quad \ldots\ldots\ldots \quad (6)$$

When p has the Lorentz value $4\pi/3$, it will be seen that α reduces to 2 and eqn. (4) to the simple Lorentz formula. For convenience we shall describe the type of dispersion formula defined by (2) and (3) as a generalized Lorentz formula, as distinguished from the simple Lorentz formula corresponding to $\alpha = 2$ in eqn. (4).

Thus any observational data on the dispersion of the dielectric constant of a dense medium can be fitted into a Drude formula, or alternatively into a generalized Lorentz formula involving any given set of polarization factors p_{ij}. This fitting into the alternative formulae can be done irrespective of what the *actual* polarization field in the medium may be, and even if there is no polarization field at all.

The equivalence of the Drude and the simple Lorentz formulae for the dispersion of the dielectric constant of a dense medium was first demonstrated by Livens (1912) for the case when the medium has a single resonance frequency, and by Herzfeld and Wolf (1925) for the case when the medium may have more than one resonance frequency. The equivalence extends, as we have just seen, also to the generalized Lorentz formula corresponding to any specified set of polarization factors p_{ij} defining the interactions between the dipole moments of the different oscillators.

This equivalence arises from the following circumstance. The effect of any polarization field that may be present in a dense medium on its dielectric constant may be taken into account in two alternative ways, which are equivalent. The effective field that polarizes the medium may be taken to include, in addition to what is usually defined as 'the field in the medium', the polarization field also, in which case the dispersion formula will be of the Lorentz type and the characteristic frequencies that appear in the formula will be the frequencies Ω_i of the individual oscillators, regarded as unaffected by the presence of the polarization field, i.e. unaffected by their mutual interactions. Alternatively one may also regard the polarization field as effective in changing the frequencies Ω_i to the corresponding resonance frequencies ω_i of the medium, and its effect on the dielectric constant as exercised indirectly through these frequencies. The result is the Drude dispersion formula. (The important part played by the polarization field in determining the infra-red resonance frequency of the alkali halide crystal, in which the polarization field involved is readily calculated, is discussed by us in a recent paper (Krishnan and Roy 1951).)

Conversely, starting with the Drude formula, and the known resonance frequencies ω_i that appear in the formula, and taking them to correspond to zero polarization field, one may postulate any desired polarization field and reduce the Drude formula to one of the Lorentz type. The frequencies Ω_i that appear in the latter formula will be different from the corresponding resonance frequencies ω_i by amounts that will be determined by the polarization field postulated.

Hence dispersion data as such can not give us any information regarding the nature of the polarization field that exists in the medium, though they enable us to obtain the resonance frequencies, directly if the data are expressed in the Drude form, since the characteristic frequencies ω_i that appear in this formula are just these frequencies, or after a simple calculation from the corresponding Ω_i if the data are expressed in the Lorentz form.

The position, however, is very different with expressions for the dielectric constant as a function of the density, where the equivalence of the Drude and the Lorentz types does not hold.

References

Herzfeld, K. F., and Wolf, K. L., 1925, *Ann. d. Physik*, **78,** 35.
Krishnan, K. S., and Roy, S. K., 1951, *Proc. Roy. Soc.* A, **207,** 447.
Livens, G. H., 1912, *Phil. Mag.*, **24,** 268.

(*Reprinted from Nature, Vol.* 170, *p.* 759, *November* 1, 1952)

Thermionic Constants of the Iron Group of Metals

In a recent communication[1], we gave an account of a new method of determining the thermionic constants of graphite, which is based on the determination of the saturation vapour pressure of the electron gas in equilibrium with the substance at different known temperatures, and application of the well-known thermodynamic relation of Clausius and Clapeyron. In the actual experiments, the saturation vapour pressure of the electron gas in a graphite chamber is determined by finding the rate of effusion of the gas into vacuum through a small hole in a thin wall of the chamber. The chamber is in the form of a thin-walled tube, and can be heated to any desired high temperature by sending a suitable heavy electric current through it. In order to eliminate the electrons emitted by the graphite surface adjoining the effusion hole, the surface is covered by a thin sheet of mica, with a small hole punctured in it; this comes just in front of a bigger one in the graphite wall and serves as the effective effusion hole.

This method of determining the thermionic constants, and in particular the coefficient A in Richardson's equation, has advantages over the other methods, since it is insensitive to the usual type of contamination of the emitting surface; and further, it does not require a knowledge of the effective area of the emitting surface or of the reflexion coefficient of the electrons at the surface.

The inner walls of the graphite chamber, as also the regions close to the effusion hole, can be coated suitably with other metals, and the method can thus be used for the determination of the thermionic constants of these metals also. We have determined in this manner the thermionic constants of chromium, iron, cobalt and nickel, depositing the metals both electrolytically and by evaporation from a tungsten wire coated previously with the metal, or carrying small rings of the metal. The results were found to be independent of the method used for the deposition of the metal and were reproducible.

The observations fit well with Richardson's equation:

$$i = AT^2 \exp(-\varphi/kT), \qquad (1)$$

in which A and φ are independent of temperature, and have the values given in the accompanying table.

Metal	φ (eV.)	A (amp. cm.$^{-2}$ deg.$^{-2}$)
Chromium	4·58 } ±0·02	60 } ±2
γ-Iron	4·31	60
Cobalt	4·41	60
Nickel	4·50	120 ±5
Note added in proof, October 8.		
Titanium	3·95	44
Vanadium	4·12	50
Manganese	3·83	34

As is well known, the observed fit of the experimental data with formula (1) with temperature-independent constants A and φ cannot be regarded as excluding a small linear variation of the actual work function with temperature, since such a variation will be equivalent to a temperature-independent change in A. Apart from the normal thermal expansion of the metal, which will lead to a small temperature variation of the work function, there is a further source of such variation in these metals. The d- and the s-energy bands of these metals overlap, the former being nearly full, and having a much larger density of energy-states than the latter. As a result, (1) the electronic specific heat in the condensed phase will be considerable, and (2) on change of temperature there will be a transference of electrons from one band to the other, and a consequent change in the work function[2]. Hence experimental data for the thermionic constants of the transition elements are of special interest.

K. S. KRISHNAN
S. C. JAIN

National Physical Laboratory of India,
New Delhi. April 15.

[1] *Nature*, **169**, 702 (1952). See also Bhatnagar, A. S., *Proc. Nat. Acad. Sci. India*, A, **145** (1944). Mathur, S. B. L., doctorate thesis, University of Lucknow (1951). Krishnan, K. S., and Jain, S. C., *Proc. Roy. Soc.*, A. (in the press).

[2] Wohlfarth, E. P., *Proc. Phys. Soc.*, **60**, 360 (1948).

Printed in Great Britain by Fisher, Knight & Co., Ltd., St. Albans.

(3)

From the Philosophical Magazine, Ser. 7, vol. xliii, p. 1224, *November* 1952.

The Temperature Variation of the Thermodynamic Potential of a Degenerate Electron Gas

By Sir K. S. Krishnan, F.R.S.
National Physical Laboratory of India, New Delhi
and
P. G. Klemens
Division of Physics, Commonwealth Scientific and Industrial Research Organization, Sydney*

[Received August 25, 1952]

In the Fermi–Dirac distribution function, namely

$$f(E)=\frac{1}{e^{(E-\zeta)/kT}+1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

ζ, as is well known, is the thermodynamic potential, or the free energy at constant pressure, per electron, and is given by

$$\zeta=u-Ts+pv, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the letters have their usual significance. Obviously ζ is a function of the temperature, and is determined by the equation

$$n=2\int_0^\infty N(E)f(E)\,dE, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where n is the number of electrons per unit volume, and $N(E)$ is the density of energy states. For an almost completely degenerate gas, i.e. at temperatures $T \ll T_0$, where

$$T_0=\zeta_0/k=\frac{h^2}{2mk}\left(\frac{3n}{8\pi}\right)^{2/3} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

is the degeneracy-temperature, the integration of (3) yields to a first approximation

$$\zeta=\zeta_0(1-\gamma T^2/6), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\gamma=\pi^2k^2/2\zeta^2. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

* Communicated by the Authors.

Since the second term in (5) is merely a correction term, ζ appearing in the denominator of (6) may be replaced by ζ_0, or by $\zeta_0{}^*$, which we shall define presently, which are both of nearly the same magnitude as ζ.

In expression (5) ζ_0 is frequently referred to as the value of ζ at $T=0$, and for that reason is sometimes regarded as independent of T, and hence the temperature variation of ζ is taken to be determined completely by the second term, which involves T explicitly. It is the main purpose of this note to emphasize that this will be the case only if the density of electrons n is kept constant, whereas at constant pressure the density n, and hence also ζ_0 as will be seen from (4), will vary with the temperature. In other words ζ_0 will not represent the free energy at the same pressure at $T=0$. The latter energy will be given by

$$\zeta_0{}^*=\zeta_0(1+\gamma T^2/3), \quad \text{. . . . . . . (7)}$$

and the expression for the temperature variation of ζ at constant pressure will therefore be given by

$$\zeta=\zeta_0{}^*(1-\gamma T^2/2). \quad \text{. . . . . (8)}$$

Physically $\zeta_0{}^*-\zeta$ has the following significance. Let ϕ_T be the thermionic work function, as usually defined, of a metal at temperature T. If the electrons in the metal, i.e. in the condensed phase, can be regarded as an almost completely degenerate assemblage, having a finite latent heat of evaporation, then the temperature variation of ϕ *due to the temperature variation of* ζ will be given by

$$\phi_T-\phi_0=\zeta_0{}^*-\zeta. \quad \text{. . . . . (9)}$$

Incidentally it may be mentioned that thermodynamically

$$\zeta_0{}^*-\zeta=T\int_0^T \frac{c_p}{T}\,dT-\int_0^T c_p\,dT, \quad \text{. . . . . (10)}$$

where c_p is the specific heat of the electrons in the condensed phase at constant pressure. In view of (8) and (10) one obtains

$$c_p=\gamma T, \quad \text{. . . . . (11)}$$

which is the same expression as for c_v.

It should be mentioned here that if the electronic structure of the metal, instead of corresponding to a nearly empty parabolic band, as we have taken it to be till now, corresponds to a nearly full parabolic band, the expressions for c_p and c_v will remain the same as before, but will now refer to the holes, and hence $\zeta_0{}^*-\zeta$ in eqns. (8), (9) and (10) should be replaced by $\zeta-\zeta_0{}^*$. In other words ζ will now increase with the increase of the temperature, though the specific heats remain positive as they should.

That in a highly degenerate electron gas, the specific heat at constant pressure should be the same as that at constant volume can also be demonstrated otherwise. At higher temperatures naturally c_p will increase more rapidly than c_v, and they will tend to the values $\frac{5}{2}k$ and $\frac{3}{2}k$ respectively per electron.