The Variation of Magnetic Double Refraction with Temperature in Acetone and Certain Acetic Esters*

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Measurement of the Cotton-Mouton coefficient at various temperatures between −60°C and 40°C were made on acetone and several normal acetic esters. Under neutral environment the relationship for these materials is best represented by a straight line with a slope of the same sign but of much larger value than can be justified by the mathematical theory. This is interpreted as indicating a larger molecular interaction in the liquid than is assumed in the theory. In the presence of a freshly cleaned surface of copper, acetone shows a reversal of sign of the birefringence with decreasing temperature. Evidence in the case of amyl acetate indicates that there is no discontinuity in the Cotton-Mouton coefficient near the freezing point.

I. INTRODUCTION

IN 1901 Kerr[2] observed that a fine suspension of iron oxide when placed in a magnetic field became birefringent. The effect disappeared when the magnetic field was removed. Later work by other investigators, among them Cotton and Mouton, demonstrated that the double refraction was associated with the particles of iron suspended in the liquid, rather than with the liquid itself.

In 1907 Cotton and Mouton[3] found that magnetic birefringence was, to a lesser degree, the property of certain organic liquids, notably nitrobenzene and others of the aromatic series. The sign of the double refraction was considered positive in the case of nitrobenzene, and negative for carbon disulphide. In 1909 the same investigators reported[4] that in nitrobenzene the variation of the magnetic double refraction over a range of temperature from room temperature upward was approximately a straight line with a slight concavity away from the temperature axis.

It was found by Cotton and Mouton that if the liquid in the magnetic field were thought of as a uniaxial crystal, of which the optic axis was parallel to the magnetic field, the magnetic double refraction could be treated exactly like a crystalline birefringence whose magnitude was proportional to the square of the magnetic field strength. If Δ represents the phase difference between the components of the emergent light parallel and perpendicular to the magnetic field, the general relationship

$$\Delta=\frac{L(n_p-n_s)}{\lambda}=C_mLH^2 \qquad (1)$$

was found to hold. Here Δ is in fractions of a wave-length; n_p and n_s are the indices of refraction parallel and perpendicular, respectively, to H; L is the length of light path in the liquid exposed to the magnetic field; λ is the wave-length in vacuum; H is the average magnetic field strength in oersteds; and C_m is the Cotton-Mouton coefficient, defined by this equation.

A mathematical theory of magnetic double refraction has been worked out by Langevin,[5] and developed and enlarged by a number of other investigators.[6] The treatment is much the same in all cases, and will not be given here. It is sufficient to point out that the orientation of the molecules by the magnetic field is assumed to be the origin of the optical anisotropy of the liquid as a whole, each molecule being assumed to have an optical anisotropy of its own which may be thought of as an ellipsoid of optical asymmetry fixed in the molecule. In addition, the important assumption is made that the intermolecular forces in the liquid are negligible.

The calculations of both Debye and Born give us, for a molecule with no permanent magnetic moment, i.e., for a molecule of a

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[1] Now at Stevens Institute of Technology, Hoboken, N. J.
[2] Kerr, Brit. Assoc. for Adv. of Sci., Reports, p. 568 (1901).
[3] Cotton and Mouton, Comptes rendus **145**, 229 (1907).
[4] Cotton and Mouton, Comptes rendus **149**, 340 (1909).
[5] Beams, Rev. Mod. Phys. **4**, 160–172 (1932).
[6] Debye, *Marx Handbuch der Radiologie*, Vol. 6, pp. 754–769; Born, *Optik*, pp. 345 ff; 360 ff.

diamagnetic substance, an expression of the form

$$C_m = A + B/T, \qquad (2)$$

in which C_m is the Cotton-Mouton coefficient; T is the absolute temperature; B is a constant which is a function *inter alia* of the magnetic polarizibility and of the optical electric polarizibility; A is similarly a function of the optical electric polarizibility, but not of the magnetic polarizibility. In Born's expression, A is small relative to B, while in Debye's relationship, A is zero.

From 1909 until 1922 little work on the variation of the Cotton-Mouton coefficient with temperature was published. In 1922 Szivessy[7] brought out the results of experiments on nitrobenzene. Szivessy's measurements were made over the range from 10°C to 60°C. These results, while confirming the theory in a general way, insofar as the value of C_m increased with decreasing temperature and showed a concavity away from the temperature axis, nevertheless were in poor quantitative agreement with the theory. The value of C_m found by Szivessy for nitrobenzene increased more rapidly with falling temperature than could be justified by Debye's equation. In Born's expression (2) Szivessy's results require the constant term to be large; a condition which this theory does not allow.

Since the work reported in this paper was begun, there has appeared[8] some data on oxygen and NO at high pressure (100 kg/cm²) and at two temperatures, 19°C and −80°C. The report cited indicates that the NO gave a thermal variation that was substantially zero between these two temperatures. The oxygen is reported as giving a variation proportional to a power of T between the inverse square and the inverse cube. The authors suggest that polymerization may play a part in the behavior of oxygen.

II. Apparatus

The apparatus employed in the present investigation consisted of the magnet and compensator described by Boorse[9] and additional equipment for controlling the temperature of the material under examination. A diagrammatic sketch of the apparatus is given in Fig. 1.

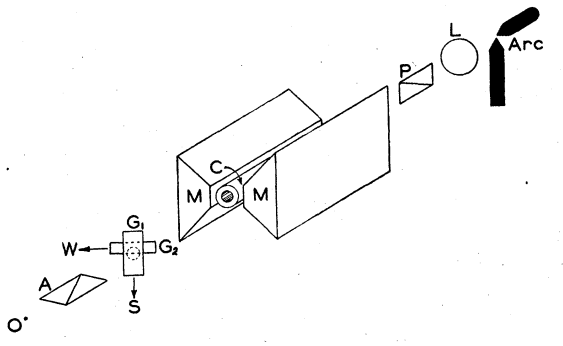

FIG. 1. Schematic diagram of the apparatus.

The source of light is the positive crater of a carbon arc. The lens system, L, produces parallel light which is polarized by a Nicol prism, P, in a plane at 45° to the axis of the magnetic field MM. The beam of light from P passes through the liquid in cell C, which is surrounded by a cooling jacket through which methanol is circulated. The means of regulating the temperature of the methanol is not shown. Upon leaving the cell, C, the light passes through the Palmer-Boorse compensator, G. This consists essentially of two glass strain-plates; G_1 covering the entire beam, and strained in a direction perpendicular to the magnetic field; and G_2 covering half the beam, and strained parallel to the magnetic field. The light finally passes through the analyzing Nicol, A, which is at right angles (optically) to P, after which it is viewed by the observer located at O. The attention of the observer is focused, by means of a telescope, on the lower edge of plate G_2.

It will be noticed that no provision has been made for providing monochromatic light for the observations. The question of what wave-length of the initial white light is effective in producing a visual image on the retina of the eye at these low intensities is one frequently raised. Under working conditions a red or a blue Wratten filter completely extinguished any trace of visual image. A good green filter of unknown history passed enough light to make the optical field barely visible, although no match could have been made at this intensity. A Wratten yellow filter (passing most of the red), produced almost no diminution in the intensity of the visual

[7] Szivessy, Ann. d. Physik **68**, 127 (1922).
[8] Bizette and Tsai, Comptes rendus **202**, 2143 (1936).
[9] Boorse, Phys. Rev. **46**, 187 (1934).

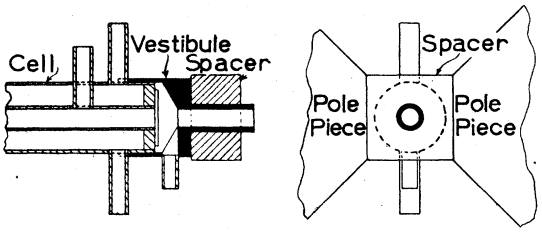

FIG. 2. Detail view of cell assembly.

field. The conclusion was reached that the effective value of the wave-length employed, even with the white source, might be taken somewhere in the green-yellow.

The manipulation of the compensator G was changed slightly from that outlined by Boorse. Briefly, the method was as follows: By means of a sliding weight on a graduated bar, the tension W on the half-shade plate G_2 could be varied continuously from zero to 250 grams. With the tension W at a convenient arbitrary value, say 100 grams, the two halves of the optical field were adjusted to match by means of the spring adjustment S on the compensator plate G_1. The two halves of the visual field then send elliptically polarized light to the analyzing Nicol. However, although the two ellipses are congruent, they are polarized in opposite directions, i.e., the conventional points tracing out the ellipses are rotating in opposite senses. The analyzer transmits only the amplitude corresponding to the direction in which it is set. In the present case it transmits a component parallel to the minor axis of the ellipse.

If we now apply the magnetic field, the two halves of the visual field become unmatched when a magnetically birefringent material is in the cell. The two halves of the field are restored to equality by sliding the weight on the bar. The amount ΔW by which the tension W is changed to restore the match is a measure of the magnetic birefringence.

The cell, by means of which the temperature of the specimen could be regulated, is shown in detail in Fig. 2. It was made of two concentric cylindrical tubes, the inner one containing the specimen, and the space between the tubes serving as a jacket for circulating the cooling methanol. The inner tube was filled through two filler-tubes passing through the jacket. One end of the cell is shown in Fig. 2 (the other end is identical). The jacket was supplied with circulating fluid through two connections at each end, as shown. The cylindrical symmetry of the cell is important in eliminating temperature inhomogeneity in the liquid specimen due to the presence of warm and cold spots in the jacket, arising from irregularities in the flow of the cooling methanol.

On the ends of the cell, which were ground parallel to each other and perpendicular to the axis of the cell, were attached thin glass windows of microscope cover glass, carefully selected for optical neutrality. The cement used to attach the windows is described by Boorse, and consists of a mixture of dextrine and *d*-mannitol. This cement remains semifluid even at relatively low temperatures, and thus does not exert an appreciable force on the windows when differential contraction between the window and the cell is brought about by a change in temperature of the cell.

Over the end of the cell is slipped a vestibule of hard rubber, shown in black in Fig. 2. This vestibule serves three purposes: (1) it provides a forespace in front of the window which is filled with evaporated liquid nitrogen introduced through the connection shown below the vestibule; (2) the opening bored in the tube, shown projecting to the right, serves as an optical stop to prevent light reflected from the inner surface of the cell from reaching the compensator and the eye of the observer; (3) the tube mentioned in (2) fits loosely into a hole drilled in the spacer-block separating the pole-pieces of the magnet, so as to support the cell properly in the magnetic field without constraint due either to the contraction arising from change of cell temperature, or due to the attraction between the pole-pieces when the magnetic field is applied.

The introduction of evaporated nitrogen into the forespace eliminates condensation of moisture on the windows, without the necessity of using double windows or other devices likely to produce optical disturbances.

The cooling methanol was introduced at one end of the cell and withdrawn at the other, thus giving the minimum of transverse temperature gradient in the specimen. The methanol was

cooled by circulating it through copper coils surrounded by solid carbon dioxide. A mixing valve enabled the amount of circulation through the coils to be regulated. The fine temperature regulation was performed by a thermostat which operated a heating coil in a reservoir through which the methanol passed.

The thermostat consisted of a resistance thermometer of 130 ohms of No. 36 nickel wire inserted in the circulating system just upstream from the cell. This thermometer formed one arm of a Wheatstone bridge, of which the adjacent arm was a variable resistor. The other two arms were fixed resistors. The temperature at which the bridge would balance was controlled by the setting of the variable resistor. The galvanometer mirror threw a spot of light onto a photoelectric cell, which in turn (through a relay circuit) reduced the current in the heating coil in the reservoir. By this means the temperature was held constant to about 0.01°C.

The temperature of the cell was determined to within a degree centigrade by means of two toluol thermometers, one located at the inlet and the other at the outlet of the cell. The difference between these two readings was less than 2°C, except at the lowest temperatures reached, at which point the difference rose to approximately 4°C. The temperature of the cell was assumed to be the mean of the inlet and outlet temperatures.

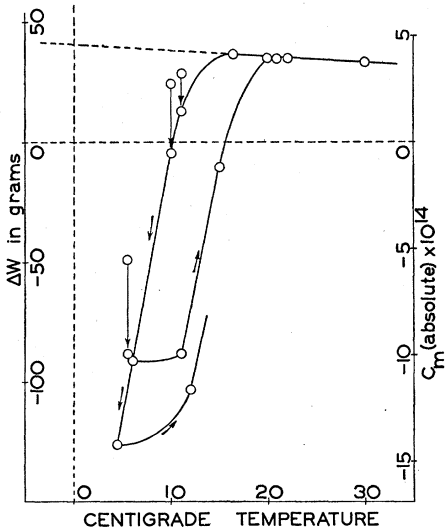

FIG. 3. C_m for acetone in the presence of freshly etched copper.

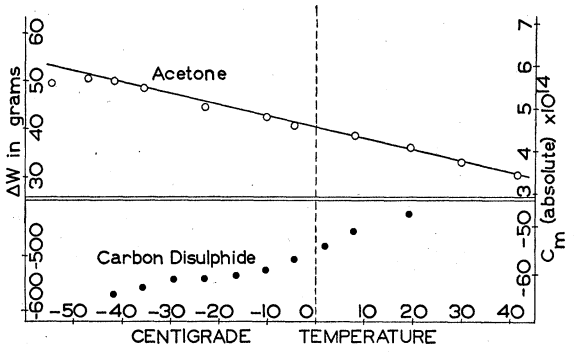

FIG. 4. C_m for acetone in aged copper and in Pyrex.

III. SPECIMEN MATERIALS

Measurements over a range of temperature from 40°C to −60°C have been made on the following organic liquids:

Acetone	Methyl Acetate	Ethyl Acetate
n-Propyl Acetate	*n*-Butyl Acetate	*n*-Amyl Acetate

A run was also made on carbon disulphide for purposes of comparison.

The acetone was technical acetone distilled three times in a Pyrex still with a refluxing column. The middle half of each run was preserved for the next distillation. The last two distillations were made over calcium chloride to remove traces of water. The esters were all from the Eastman Kodak Company Research Laboratory, and were all redistilled before using.

IV. RESULTS

The first thing to point out under this heading is the existence of an interaction between the material of the cell and the specimen. This interaction was most pronounced in the case of a copper cell carefully cleaned with a solution of hydrochloric acid and then thoroughly rinsed with distilled water, then with acetone, and finally with large amounts of the acetone to be studied. The values of C_m for acetone in the copper cell so treated, are given in Fig. 3. The fact that the two branches of the curve (one taken with decreasing temperature, and the other with rising temperature) happen to rejoin at slightly below room temperature, rather than at some other temperature, may be characteristic of acetone, as there is some indication that the other materials studied formed loops

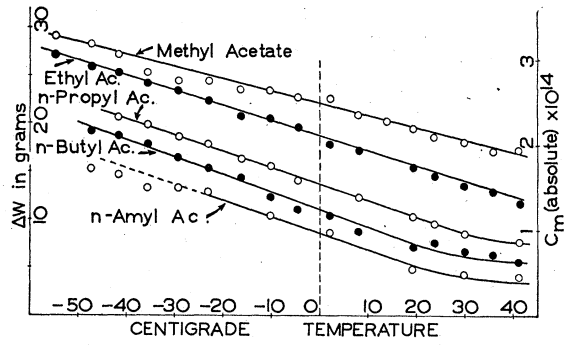

FIG. 5. C_m for certain acetic esters.

rejoining at considerably lower temperatures. This type of behavior was first noticed in a newly-made brass cell, and caused the abandonment of brass in favor of copper; the copper however showed the same effect when it was new, but gradually over a number of days of use, the loops became less and less steep until at last no reversals took place and the variation of the Cotton-Mouton coefficient with temperature took on the form shown in Fig. 4.

In order to determine which type of relationship represents the action of acetone and other materials in a neutral environment, a Pyrex cell was constructed of the same form as the metal cell described above and shown in Fig. 2. Acetone and methyl acetate were measured in this cell and gave values in agreement with the curves of Figs. 4 and 5, within the limits of experimental error (±5 percent). The experimental error was larger in the glass cell on account of a greater thermal inhomogeneity in the liquid arising from the lower thermal conductivity of the glass compared to copper. In addition, the magnetic birefringence was partly masked by a Faraday effect due to the fact that unavoidable inaccuracy in the shape of the glass cell caused it to lie with its axis not quite perpendicular to the magnetic field. Enough precision was obtained, however, to verify the agreement between the curves in glass and in aged copper.

The values upon which the curves of Figs. 4 and 5 are based are given in Table I. Each value is the mean of several determinations. No value is based on fewer than 20 determinations, and in the case of acetone the mean of as many as 130 determinations is used for several of the points. It will be noticed that with the possible exception of the higher esters, the concavity upward, which Szivessy, and Cotton and Mouton, found in nitrobenzene, is not present. In the three esters which may show such a curvature, it exists, if at all, only at the higher temperatures.

The precision of these measurements of ΔW is estimated to be better than ±0.5 gram. The total spread of the individual readings for each point is of the order of ±2.5 grams.

The values of ΔW given in Table I can be converted into C_m in absolute units for substitution in expression (1) given earlier in this article, by multiplying ΔW by the factor 0.11×10^{-14}. This factor is obtained by standardizing $\Delta W = 35.6$ grams at 20°C as equivalent to $C_m = 3.9 \times 10^{-14}$, and taking the factor of proportionality.

Amyl acetate apparently supercooled considerably to reach the lowest temperature on its curve. At −48°C the cell containing the amyl acetate was slightly disturbed, whereupon the liquid became completely opaque. The temperature of the cell was then slowly raised to approximately −30°C, at which point melting began to be apparent. A small amount of light could be seen through the liquid, but the path was partially obscured by a large number of needle-like crystals. On further warming these crystals disappeared in the neighborhood of −20°C. Recooling, after this, led to freezing in the

TABLE I. *ΔW in grams. $C_m = \Delta W \times 0.11 \times 10^{-14}$ where C_m is the Cotton-Mouton coefficient.*

Degrees C	Acetone	Methyl Acetate	Ethyl Acetate	*n*-Propyl Acetate	*n*-Butyl Acetate	*n*-Amyl Acetate
41.0	30.4	17.1	11.6	7.6	5.6	4.0
35.8		17.0	12.8		6.3	
29.8	33.2	18.0	13.4	8.4	6.7	4.2
23.5		18.6	14.3	9.5	7.5	
19.1	36.2	19.4	15.3	10.2	7.1	4.8
13.5		20.2				
7.9	38.9	20.9	17.1	12.2	8.6	
1.9		22.6	17.9		10.2	8.6
−4.8	40.9	22.7	19.6	14.0	10.9	
−10.4	42.5	23.4	20.4	15.5	12.2	10.3
−16.6		23.5	20.7	16.2	14.3	
−23.2	44.7	24.3	22.2	17.7	15.1	12.7
−29.4		24.4	23.4	18.5	16.3	13.1
−35.8	48.5	25.3	24.1	19.8	17.8	13.1
−41.8	50.0	27.1	25.2	20.5	18.7	14.5
−47.4	50.5	28.2	25.9	20.2	19.1	15.1
−54.8	49.6	29.1	27.1			

neighborhood of −30°C repeatedly, without any further supercooling. It is interesting to note a suggestion of a plateau in the neighborhood of −30°C on the curve, (Fig. 5) although the magnitude of the effect is small and may not be significant.

One effect was very pronounced in the amyl acetate below −30°C, however. The lens action (due to a difference in refractive index caused by a temperature difference between the liquid near the wall of the cell, and the liquid on the axis of the cell) became very large below the apparent freezing point. In fact, on looking through the cell as the temperature was being lowered, the distant cell window, which ordinarily at such times appeared only slightly reduced in angular size, had in this case dwindled to the apparent size of a pinhole.

It is safe to say, however, that there is no marked change in the magnetic birefringence of amyl acetate in the neighborhood of its freezing point.

V. Discussion

The results of this investigation, as in the case of that of Szivessy, cannot be reconciled with the predictions of either Born or Debye, and the conclusion seems inevitable that the discrepancy between theory and experimental fact must be ascribed to intermolecular energies neglected in the theory. This thought led to the question of whether the disagreement should be ascribed to the complexity of the organic molecules involved in the action or whether it was due merely to the liquid state. To answer this, a run was taken on carbon disulphide (Eimer & Amend, C.P. redistilled). Carbon disulphide is the simplest molecule showing marked magnetic double refraction. The results are given as a part of Fig. 4. It is to be noted that C_m for carbon disulphide is large negatively, and is plotted here merely for comparison. It is clear that the agreement with the theory is, if anything, worse than for acetone. It therefore seems safe to say that the theory is not applicable to liquids.

On the subject of the loops traced by C_m for acetone and methyl acetate in the presence of etched copper, further investigation must precede an explanation. There are, however, two possibilities to be considered: (1) the formation of metal-bearing molecules with the acetone or methyl acetate; (2) the catalytic action of a fresh surface of the metal causing molecular aggregation in the acetone. In connection with these two possibilities there are several observed facts to be considered, namely: (1) when copper-oxide powder is added to the acetone showing the loop, the loop is altered so that ΔW remains positive over the entire temperature range; (2) when the curve is a loop, the time for the birefringence to disappear after the magnetic field is removed becomes quite long at low temperatures, rising in some cases to as much as 30 seconds (when the curve is a straight line, the relaxation time is quite short—of the order of $\frac{1}{2}$ second—and is apparently independent of the temperature); (3) the equilibrium values from which the upper branch of the curve in Fig. 3 was plotted were obtained only after a wait of several minutes. This is indicated by the arrows which connect the initial values with the final stable values at each temperature.

It should be pointed out here that in the work of other investigators the effect on the value of the Cotton-Mouton coefficient, of interaction between the acetone and the material of the cell has not been mentioned. Most of the measurements have been made in brass cells. While it seems likely, in the light of the present investigation, that acetone and the acetic esters give satisfactory results in a properly matured metal cell, it is possible that the disagreement between various investigators[9] on the values of C_m for the alcohols is due to an interaction between the alcohol and the material of the cell.

During the investigation of the literature for data covering the optical behavior of acetone and the esters, it was noticed that there is a large gap in the data on the index of refraction of liquids below room temperature. The experience gained in this investigation shows that technically such measurements would be difficult to make, but they should be by no means impossible, and it seems quite possible, in view of the behavior of the thermal coefficient of the refractive index of amyl acetate below −30°C, that the field would yield data of interest.

In closing I would like to express my appreciation and gratitude for the kindness of the late

Professor A. P. Wills in placing the compensator and the electromagnet at my disposal, and for his encouragement during the period of apparatus development. I wish to thank, also, Professor D. P. Mitchell whose suggestions have contributed largely to the satisfactory solution of the problem of the temperature control of the cell. Professor H. W. Farwell has been a valuable aid through his continuous interest and his technical advice on the details of the investigation.

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Internal Friction in Solids

II. General Theory of Thermoelastic Internal Friction

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Stress inhomogeneities in a vibrating body give rise to fluctuations in temperature, and hence to local heat currents. These heat currents increase the entropy of the vibrating solid, and hence are a source of internal friction. The general theory of this internal friction is here developed. The simplest example of stress inhomogeneity is that occurring in the transverse vibrations of reeds and wires. Explicit formulae are obtained for reeds and wires, and the effect is calculated of crystal orientation in single crystal specimens. Microscopic stress inhomogeneities arise from imperfections, such as cavities, and from the elastic anisotropy of the individual crystallites. The internal friction due to spherical cavities is calculated. The internal friction due to elastic anisotropy is investigated for cubic metals, and is found to be greatest for lead, least for aluminum and tungsten.

§1. INTRODUCTION

IN a recent paper[1] the writer investigated theoretically that part of the internal friction of a vibrating reed which arises from the flow of heat back and forth across the reed. On comparing the calculated values of this thermoelastic internal friction with the experimental values of internal friction for longitudinal vibrations in rods, he predicted that over a wide frequency band the internal friction in reeds due to this thermoelastic effect was of a larger order of magnitude than that due to all other causes. In the succeeding paper an experimental verification of this prediction will be presented. The striking agreement of prediction with experiment renders it opportune to investigate more thoroughly the thermoelastic effect. Such an investigation is here undertaken.

This paper begins with a generalization of the analysis given in reference 1 for transverse vibrations (§2). It is found that for a rod of arbitrary cross section vibrating transversely, with frequency ν,

$$Q^{-1}=\frac{E_S-E_T}{E_S}\cdot\frac{\nu_0\nu}{\nu_0^2+\nu^2}. \tag{1}$$

Here E_S is the adiabatic Young's modulus, E_T the isothermal modulus, both measured along the axis of the wire. In the case of a rectangular cross section (reed), the frequency for maximum Q^{-1}, ν_0, is given by

$$\nu_0=(\pi/2)Dd^{-2}.$$

Here D is the thermal diffusion constant of the material, d is the width of the rod in the plane of vibration. In the case of circular cross section (wire),

$$\nu_0=0.539Da^{-2},$$

where a is the radius of the rod, or wire. Eq. (1) is valid for both isotropic and anisotropic rods. Tables are given to show the dependence of $(E_S-E_T)/E_S$ upon crystal orientation in single crystal rods. It is predicted that the internal friction in single crystal zinc rods will vary radically with crystal orientation, differing by a factor of seven for parallel and normal orientation.

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[1] C. Zener, Phys. Rev. **52**, 230 (1937).