Measurement of the Internal Friction of Solids

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VERY limited work has been done on internal friction by transverse vibrations at frequencies in the sonic and infrasonic range. The only important investigation in this respect is perhaps that of Bennewitz and Rötger.[1]

In the present inquiry, the internal friction of a number of solids in the form of wires having diameters or thicknesses between 0.025 cm and 0.1 cm, and lengths between 1 cm and 15 cm, was determined from transverse vibrations at frequencies between 10 and 1000 c.p.s. Two methods were employed *viz.*, the decay of free lateral vibrations and the width of resonance.

In the case of insulating materials, damped vibrations were initiated by gentle blows. In the case of conducting materials, damped as well as maintained vibrations were excited by electrostatic means. Experiments were carried out at a pressure of 0.001 cm. of mercury, and the maximum amplitudes were of the order of 0.0005 cm. and were estimated from the depth of the modulations introduced by the vibrating end of the wire on an intense beam of light. A photoelectric cell circuit incorporating a low noise amplifier, a cathode-ray tube, and a beat-frequency oscillator were used to detect and measure the vibrations. Oscillograms of damped vibrations were obtained by a moving film.

Experiments show that, even at low air pressure, the presence of boundaries near the vibrating specimen increases the decrement appreciably unless the distance is greater than about 0.5 cm. The behavior of steel, zinc, lead, glass, brass, and tin as regards the existence of a frequency corresponding to a maximum value for the internal friction confirms Zener's theory,[2] which attributes the internal friction in polycrystalline solids primarily to thermal currents. The curves in Fig. 1 give a summary of the results. The position of the calculated maxima are marked by vertical lines. Steel shows two maxima, the first of which is probably due to the contribution of ferromagnetism.

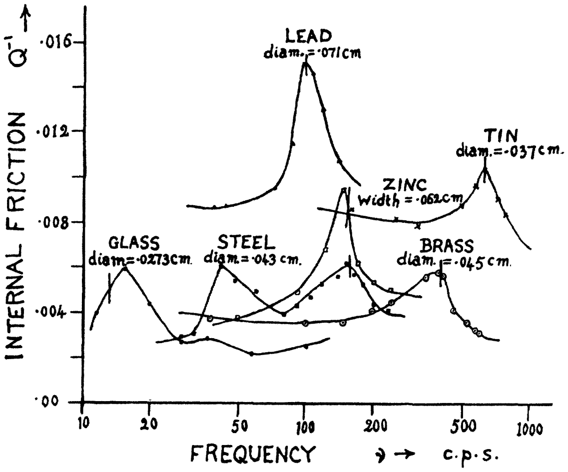

Fig. 1.

It has been observed that the transitional elements, nickel, palladium, and platinum, when subjected to forced vibrations, show two closely coupled maxima in the resonance curves from which it was not possible to calculate the internal friction.

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Absence of Photo-Conductivity in Tungstate Phosphors

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SCHEELITE ($CaWO_4$) has recently received considerable attention because of its efficiency in scintillation counting applications.[1] The tungstates are furthermore of general interest since they are among the comparatively few "pure" materials that give efficient room-temperature luminescence.[2] The similarity of the emission spectra of various tungstates strongly suggests that the tungstate ion is the luminescent center, and recent work by Kröger[3] gives added support to this viewpoint. Because of the rapid decay of the tungstate fluorescence ($\sim 10^{-6}$ sec.) it has generally been assumed that absorption of ultraviolet radiation, at least in the region of the first lattice absorption bands, produces only excitation of the tungstate ion, and that free electrons are not formed. Randall and Wilkins,[4] however, claim to have found photo-conductivity in pressed powders of $CaWO_4$ under 2650A and 3650A excitation, an observation which calls for a revision of the tacitly accepted picture of tungstate absorption and luminescence.

Since synthetic single crystals of a few efficient tungstate phosphors have recently become available,[5] it was thought worth while to search for photo-conductivity in these crystals. Crystals of $CaWO_4$ and $CdWO_4$, grown from the melt by the Crystal Section, NRL, and a crystal of $CaWO_4$ grown by the Linde Air Products Company were examined. Excitation, emission, and absorption spectra were also measured on the same crystals used in the photo-conductivity experiments.

For investigation of the photo-conductivity over the range 2200A to 4000A the light source was a hydrogen discharge lamp, the radiation being dispersed by a Gaertner quartz monochromator. Spot checks at 2537A were also made using a low pressure mercury arc lamp focused directly on the crystals. Care was taken to avoid illuminating the electrodes with the exciting light, because experiment indicated that spurious photo-currents resulted when the electrodes were irradiated with ultraviolet. The use of carbon electrodes, rather than metallic ones, was likewise found necessary in order to eliminate a small amount of photo-emission from the electrodes. With these precautions no photo-current was observed in either $CaWO_4$ or $CdWO_4$, with 225 volts applied to the crystals, using an instrument capable of detecting 5×10^{-15} ampere. This current is less than one-thousandth that observed with the photo-conductive crystals AgCl and TlCl under similar conditions.

Randall and Wilkins have also reported that $CaWO_4$ is faintly luminescent under 3650A excitation. We observed no luminescence in powders or single crystals of this material by visual or photographic examination under radiation from a "360BL" lamp equipped with an appropriate filter (Sylvania "Blacklight" lamp).

The excitation spectrum of $CdWO_4$, uncorrected for the energy distribution of the hydrogen lamp or for the transmission of the monochromator, has a peak at 3100A and a long-wave-length limit of 3350A. The excitation spectrum of $CaWO_4$, likewise uncorrected, peaks at 2600A and has a long-wave-length limit of 2850A. Kröger[3] reports an excitation limit of 2600A for pure $CaWO_4$, which shifts to about 3000A on the addition of 1 mole percent of lead. We therefore suspected lead contamination in our single crystals of $CaWO_4$. Spectroscopic analyses, capable of detecting 0.008 mole percent of lead, showed no lead in these crystals, however. Furthermore, a transmission spectrogram of one of the $CaWO_4$ crystals showed an absorption edge at 2720A with a long-wave-length extension of the edge to about 2800A, in fairly good agreement with our excitation data.

Our experiments indicate, then, no basis for concluding that free electrons are produced when tungstates are excited by ultraviolet light. The 3650A-excited luminescence and the photo-conductivity of $CaWO_4$ observed by Randall and Wilkins may have been due to impurities. Also, photo-emission for the electrodes may have played a part in their photo-conductivity measurements.

We wish to thank Esther W. Claffy for the spectrographic analyses; Robert J. Ginther for the transmission spectrogram of $CaWO_4$; and Stewart Slawson for the cutting and polishing of the crystals. Acknowledgment is also expressed to the Linde Air Products Company for their kindness in providing a specimen of their synthetic scheelite.

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Infra-Red Absorption of Oxygen and Nitrogen Induced by Intermolecular Forces

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An unperturbed homonuclear diatomic molecule can exhibit no rotation-vibrational absorption due to dipole transitions. However, in an attempt to detect $(O_2)_2$ complexes by infra-red absorption, we have found in liquid and compressed gaseous oxygen a marked absorption with a maximum at the vibrational frequency of the O_2 molecule, 1556 cm^{-1}. An investigation of compressed gaseous nitrogen showed a similar absorption at the N_2 vibrational frequency, 2331 cm^{-1}. The intensity-pressure relationships for both gases and for mixtures of the two gases prove conclusively that the absorption cannot be due to stable complexes or to quadrupole transitions. The effect must have its origin in dipole transitions induced by intermolecular forces during collisions.

The absorptions of the gases at pressures up to sixty atmospheres in a path length of 85 cm were measured with a Perkin-Elmer spectrometer. For pure oxygen at constant temperature, the absorption coefficient at all frequencies in the band was found to vary as the square of the pressure, as shown for two frequencies in Fig. 1. The shape of the absorption band, absorption coefficient *vs.* cm^{-1} (Fig. 2), is therefore independent of pressure. When nitrogen is added to the absorption cell and the partial pressure of oxygen is held constant, the oxygen absorption increases linearly with the partial pressure of nitrogen. The absorption observed in pure nitrogen has approximately the same intensity and shape as the oxygen band. In this case also, the absorption coefficient increases as the square of the pressure.

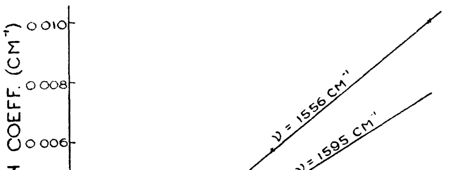

FIG. 1. Variation of the absorption coefficient with pressure at two points in the oxygen band.

These results are immediately explained on the assumption that the molecule absorbs during a collision with either a like molecule or a foreign gas molecule. The perturbation of the molecule by the strong intermolecular forces effective during the collision must produce a finite transition probability. Condon[1] has shown that the dipole induced in a molecule by a static electric field should give rise to transitions obeying the Raman rather than the infra-red selection rules. The polarization of the molecule by a colliding molecule will undoubtedly produce the same effect. Thus, the intensity distribution for the induced absorption in oxygen should be given by the Raman selection rules for rotation, $\Delta J=0, \pm 2$. This is compared with the experimental curve in Fig. 2. The envelope of the theoretical *O*- and *S*-branches matches well the intensity contour in the wings of the band. The integrated intensity of the *O*- and *S*-branches is found to be 0.7 of the total intensity of the band. This is very close to 0.75, the value of the theoretical ratio for the anisotropic part of the Raman scattering for a diatomic molecule. There seems, therefore, to be very little intensity in the *Q*-branch corresponding to isotropic Raman scattering. The intensity contour observed for liquid oxygen is consistent with that observed for the gas when the change in the Boltzmann factor with temperature is taken into consideration.

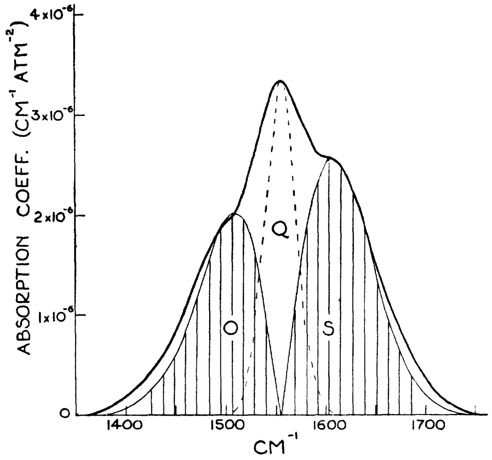

FIG. 2. The induced rotation-vibrational absorption of gaseous oxygen. The heavy curve is the experimental contour; the light curve is the theoretical envelope of the *O*- and the *S*-branch. The residual, *Q*-branch, intensity is shown as a broken line.

Discrete rotational lines were not observed. This is not unexpected, since the collisions postulated for the origin of the band should broaden the lines considerably. It is significant that the perturbation is sufficient to alter the transition probabilities but has negligible effect on the vibrational frequency.

The induced absorption established here should be a characteristic property of all molecules but is, of course, most readily detected for vibrations which are not otherwise infra-red active. It is probable that the infra-red absorption in hydrogen reported by Herzberg,[2] and attributed by him to quadrupole transitions, is due in part at least to induced transitions. The quadrupole intensity would introduce a linear term in the variation of the absorption coefficient with pressure. There seems to be an indication of this quadrupole term in oxygen at low pressures (Fig. 1).

* Holder of a scholarship under the Ontario Research Council, 1947–49.

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