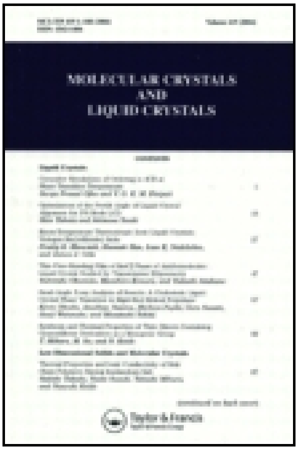

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Internal Magnetic Viscosity in Dielectric Materials Induced by Paramagnetic Centers

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Internal Magnetic Viscosity in Dielectric Materials Induced by Paramagnetic Centers

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A torsion pendulum is constructed by suspending a sample from a quartz fiber, and the damping constant of torsional oscillation is measured. Damping is observed depending on the strength of an applied magnetic field for a variety of substances which have been thought to be "pure diamagnetics". This effect is attributed to the presence of small amounts of ions or molecules which carry unpaired electrons. This point of view is illustrated with the examples of $CaCO_3 \cdot Mn^{2+}$ and KCl crystals containing *F* centers, and also by means of solid solutions of the DPPH free radical in paraffin wax.

INTRODUCTION

It has been reported in a previous paper[1] that the damping constant resulting from the decrease of the amplitude of angular oscillations of a diamagnetic sample in a homogeneous magnetic field depends on the field strength, H. This remarkable fact, which has been attributed by other authors to the presence of ferromagnetic inclusions in samples of natural quartz,[2] is also true with respect to a variety of solid and liquid substances which can safely be assumed to be free from ferromagnetic contamination. By contrast, we believe that the observed damping constant, with a broad maximum for some value of the field strength, H_{max}, is characteristic for substances doped with impurities which do possess electrons with unpaired spins. In such experiments described first by Braginskii *et al.*,[2] the crystal (or pulverized substance enclosed in a thin-walled glass container) is suspended on a thin quartz fiber in a horizontal and homogeneous magnetic field. The amplitude of angular vibrations around the vertical axis diminishes stepwise, and the damping constant of this process, β_r, can be measured as a function of H. β_r denotes the reduced value of the damping constant[1]

$$\beta_r(H) = \beta(H) - \beta(0).$$

In this paper, we will try to exemplify the influence of paramagnetic centers on the magnetic viscosity of the substance, represented by the value of $\beta_r(H)$, by a number of examples including inorganic and organic substances, in both liquid and solid phases.

EXPERIMENTAL

All experiments were performed at room temperature using the apparatus shown schematically in Figure 1. The sample is attached to the quartz filament by means of a small piece of thin glass rod holding a small mirror. The reflected light beam monitors two photo-transistors placed on a curved scale at a fixed angular distance. The period of time, Δt_n, which is required for the beam to pass between the two transistors is measured. For increasing values of the integer, n, which counts the subsequent passages of the beam, Δt_n increases according to the relation

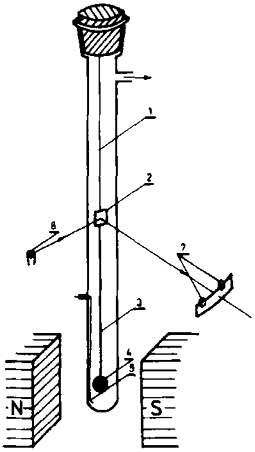

FIGURE 1 Aparatus (schematic). 1—quartz filament, 2—small glass mirror, 3—glass bar (rigid), 4—sample, 5—thermocouple, 6—lamp, 7—scale and phototransistors.

$$\ln \sin\left(\frac{2\pi}{T}\,\Delta t_n\right) = \beta[(n - 0.25)T + \Delta t_n] + A.$$

This relation holds provided that the first of the two transistors is placed exactly in the position which the light beam strikes with the mirror at rest. T and β are the mean period and the damping constant of the oscillations, respectively, A is a constant, the numerical value of which does not need to be known here and $n = 1, \ldots, 21$. From 21 values of Δt_n, β is determined from a least-squares fit. The accuracy of the time measurement was 1 millisecond. The mean weight of samples used was about 100 milligrams. A typical period of vibrations ranged between 1.0 and 1.5 seconds. All measurements were carried out in a vacuum, $\sim 10^{-3}$ mm Hg. A magnetic field was applied in the range of 0 to 0.7 tesla, and the field strength was measured by means of the Hall effect.

"PURE DIAMAGNETICS"

In the investigation of the behavior of a variety of substances, it was found that the dependence of β on the magnetic field strength is a common feature of a great number of substances. This was rather unexpected because, for a diamagnetic which is a chemically homogeneous substance, there is no reason for β to depend on H. The diamagnetic susceptibility is a field-independent material constant over a wide range of field strengths. Therefore, at the beginning of the investigation, two principal questions had to be answered:

(i) Is it possible to find a substance which is an intrinsically pure diamagnetic? By this term is meant a substance for which β is field-independent.

(ii) Which factors or material properties may be responsible for the characteristic $\beta_r(H)$ behavior of the great majority of substances?

The results of the experiments are shown in Figures 2 and 3. The figures present the reduced damping constant, β_r, as a function of the magnetic field strength. Let us consider first curves 1, 2 and 3 in Figure 2, corresponding to NaCl crystal, liquid water and liquid benzene, respectively. All these three substances are magnetically isotropic and seem to meet the properties anticipated for pure diamagnetics, al-

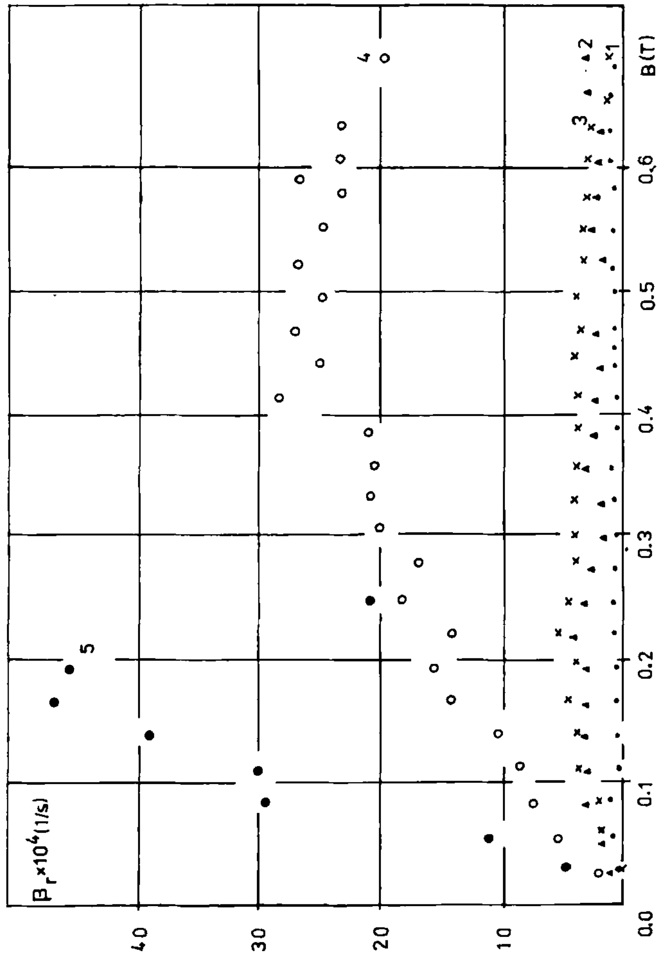

FIGURE 2 Damping constant as a function of the magnetic field strength. Curve 1: pure NaCl, 2: distilled water, 3: liquid benzene, 4: KCl.F, 5: solution of DPPH in toluene.

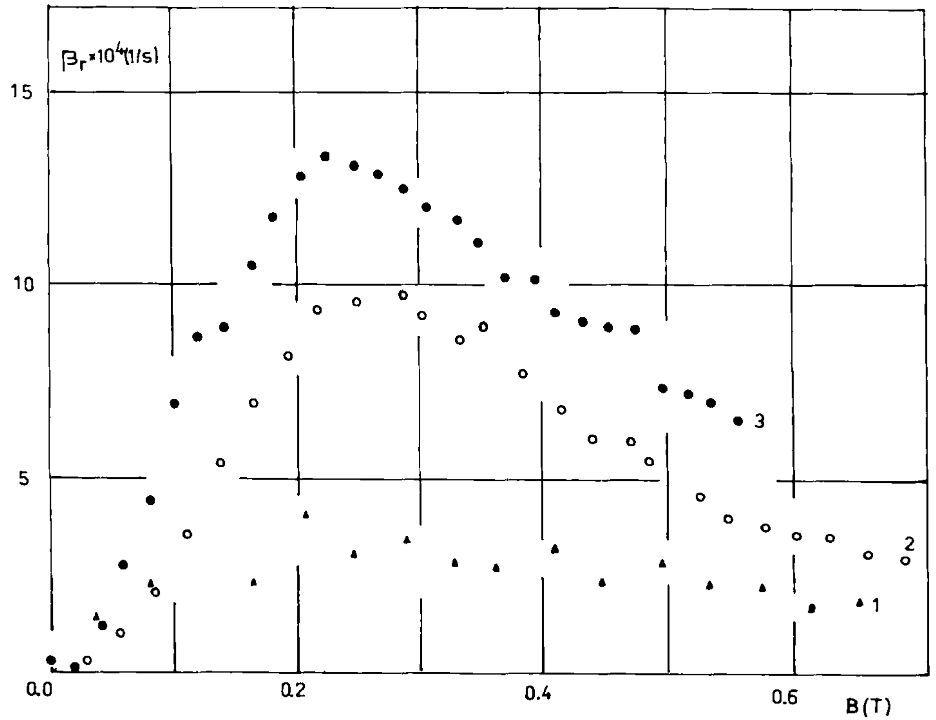

FIGURE 3 Damping constant as a function of the magnetic field strength. Curve 1: pure anthracene, 2: natural calcite suspended perpendicular to the three-fold axis, 3: natural calcite suspended perpendicular to the cleavage plane.

though only the NaCl crystal is nearest to this ideal case. It is worthwhile mentioning, however, that the results shown by curve 1 were obtained for a sample carefully selected from among crystals of various origins which, as a rule, showed very different behavior in the magnetic field. Let us also observe that the physical state of the sample is of little significance in the rate of loss of the total energy of libration in the magnetic field. Therefore, hydrodynamic effects due to mechanical viscosity of the liquid and/or its change in the magnetic field are rather small, even in those liquids whose molecules have large anisotropy in diamagnetic susceptibility (benzene). A somewhat larger scale of changes in β_r was found in anthracene crystal, curve 1 in Figure 3, in spite of the fact that this crystal was grown from the melt made from a very carefully purified substance (~three-fold crystallization from toluene, and vacuum sublimation followed by zone-melting with about 100 passages of the zone). The discrepancy between the anticipation and experiment may in this case be explained by the known ability of anthracene to form oxidation products by surface adsorption of oxygen and/or its photochemical activity under ultraviolet radiation.[3]

Much stronger field effects were found in crystals of natural calcite, $CaCO_3$, curves 2 and 3 in Figure 3. If we agree that an increase of the damping constant for higher fields is due to the presence of a certain number of unpaired spins, we would have to assume a contamination of calcite with foreign ions having unpaired electrons. This is not impossible because natural calcite can contain a certain amount of impurity ions, e.g., Mn^{2+}, of a size and valency suitable to replace Ca^{2+} ions in the host lattice. As a matter of fact, a spectrographic emission analysis carried out for this substance gave the following results (in percent): Si: $10^{-4} - 10^{-3}$; Mg: 10^{-3}; Mn: 10^{-2}; Fe: 10^{-4}; Al: 10^{-3}; Cu: 10^{-4}. Therefore, the deviation of calcite from ideal behavior is most probably due to the presence of Mn^{2+} ions in a concentration of about 10^{-2} percent. In these crystals, a small anisotropy effect was also observed: the results for a calcite plate suspended perpendicular to the three-fold symmetry axis of the crystal (curve 2 in Figure 3) differ slightly from those obtained for the same plate when it was suspended perpendicular to the cleavage plane (curve 3 in Figure 3).

In conclusion, we suggest that a large number of substances which are thought to be "pure" diamagnetics are, in fact, contaminated with minute amounts of foreign ions which carry unpaired electrons. Among the substances investigated so far, only selected samples of NaCl and pure paraffin wax (cf. next paragraph) are free from paramagnetic admixtures.

SUBSTANCES DOPED WITH UNPAIRED SPINS

The conclusions which were reached in the last paragraph have led to another question: what would be the behavior of a sample that contained some amount of deliberately introduced unpaired spins?

Three substances were chosen to answer this question.

(i) A KCl crystal containing *F* centers. These centers are formed by single electrons trapped in anionic vacancies. The electrons can be introduced into the lattice by heating the KCl crystal in the presence of potassium vapor. In the crystal used, the concentration of *F* centers amounted to, approximately, $4 \cdot 10^{17}$ cm^{-3}. Experimental results are shown in curve 4 in Figure 2. This curve has a maximum at $H = 0.5$ tesla and is situated considerably higher than the curves corresponding to the pure substances.

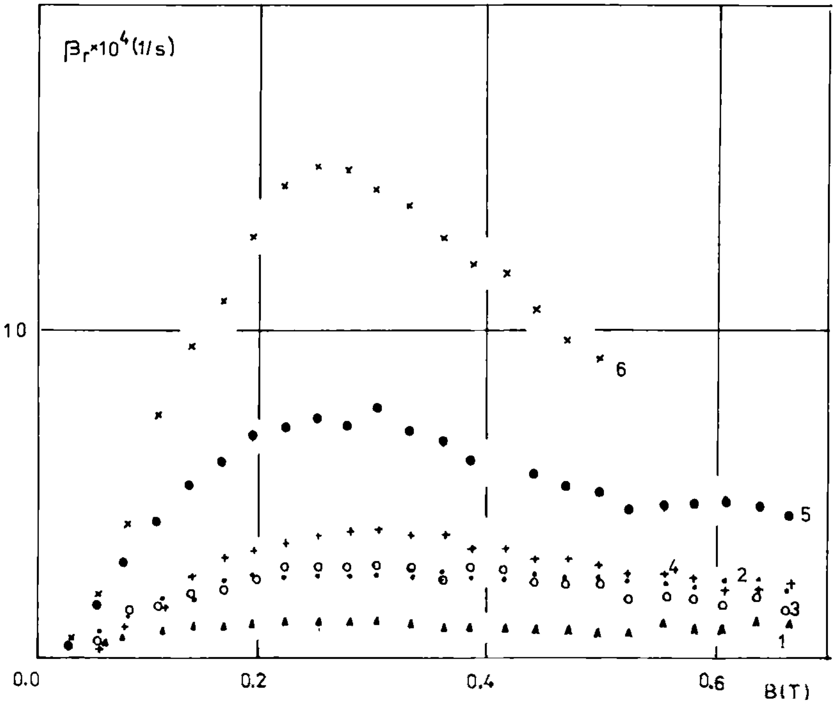

FIGURE 4 Damping constant as a function of the magnetic field strength for solid solutions of DPPH in paraffin wax. Concentrations in units of $a = 10^{-5}$ g/g. Curve 1: 0, 2: 2a, 3: 4a, 4: 6a, 5: 8a, 6: 10a.

(*ii*) As the second substance, a toluene solution of the radical diphenyl-picrylhydrazyl (DPPH) was prepared with a certain amount of polystyrene dissolved in the same solvent. The polymer was added to diminish possible hydrodynamic effects in the β measurements. The experiments could not have been carried out over the whole range of field strength because of very high damping effects at higher fields (curve 5 in Figure 2).

(iii) More quantitative experiments were carried out with solid solutions of DPPH in a mixture of aliphatic hydrocarbons, the so-called paraffin wax. This substance, although chemically not homogeneous, can be obtained in a state of good physical purity, as is demonstrated by the very small β values (curve 1 in Figure 4). Other curves in the same figure illustrate the behavior of solid solutions with an increasing content of DPPH. A plot of β_{max} against concentration is shown in Figure 5.

The content of DPPH in the sample of highest concentration was determined by weight. Other samples were obtained by dissolving a known weight of the first sample in known amounts of solvent. Solu-

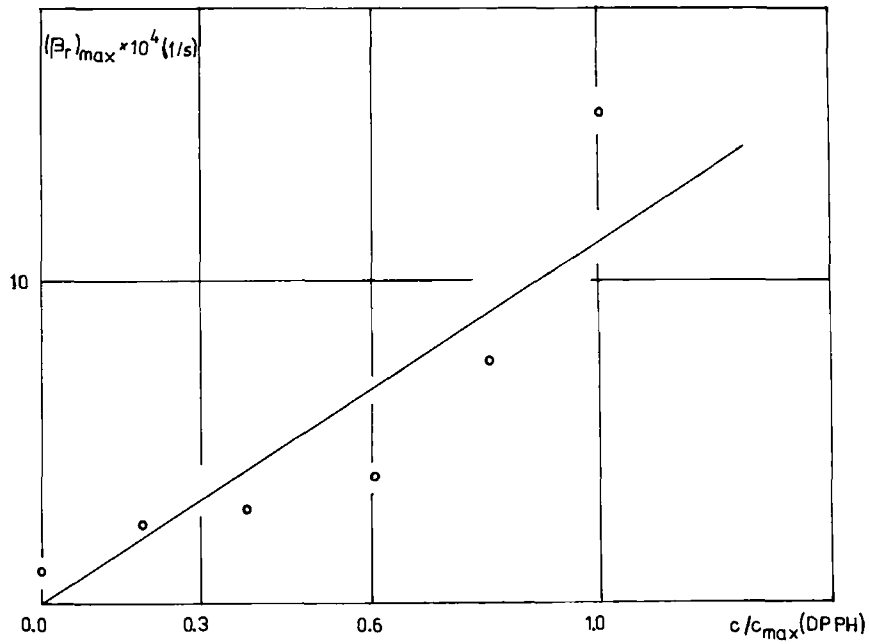

FIGURE 5 Concentration dependence of (β_r) max for solid solutions of DPPH in paraffin wax.

tions were prepared in liquid paraffin wax kept at a constant temperature of 50° by means of a water bath. Because of the small amount of the radical used, the concentration is not accurately known. An additional uncertainty can arise from the fact that partial deactivation of DPPH may occur due to heating. Therefore, an independent control of the concentration of DPPH seemed to be indispensable. This was accomplished by means of electron spin resonance measurements using an ESR spectrometer made in the Institute of Telecommunication and Acoustics of the Technical University of Wroclaw. Its resolving power, as claimed by the designer, is equivalent to the presence of about 10^{11} spins in the sample.

Unexpectedly, only the sample of the highest concentration gave an ESR signal of an amplitude significantly greater than that of the empty scan of the glass container and the microwave cavity, (Figure 6). This discrepancy between the concentration of DPPH determined by weight and the number of detectable spins can be explained by the fact that the DPPH used could have been greatly deactivated because of a prolonged storage time. Some additional deactivation that could happen during heating at 50° was mentioned earlier. Also the true resolving power of the spectrometer seems to be much lower than that given by the designer. A more precise comparison of the sensitivity of both

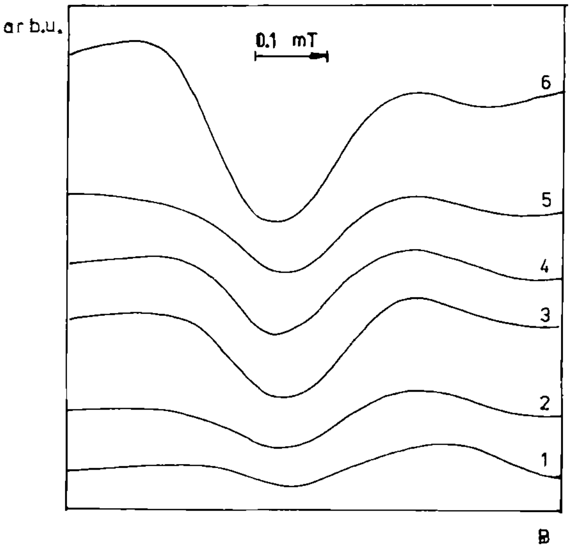

FIGURE 6 ESR signals for samples corresponding to Figure 4.

experimental methods with the presence of free radical molecules is necessary and will be undertaken in the near future.

The results of the experiments described here seem to point to the fundamental role of unpaired electron spins in the internal magnetic viscosity of solids as measured by means of damping effects in a magnetic field. The unpaired spins can either be introduced into an inorganic substance by means of suitable ions, or by dissolving free radical compounds in appropriate solvents.

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