

# Aromagnetism: A new type of magnetism

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A fundamentally new type of permanent magnetism has been observed. It is found in a wide class of organic substances in the form of a suspension of small crystals in a liquid (in particular, in water). The constant magnetic moment is proportional to the volume of these crystals.

Small crystals of several aromatic substances distinguished by a planar structure of the molecules, without substituents in their rings [anthracene, phenanthrene, pyrene, *p*-terphenyl, triphenylene, naphthalene, perylene, picein, pentacene, benz(*ghl*)perylene, 1,2,6,7-dibenzoperylene, and also azulene] exhibit some previously unseen magnetic properties, which we refer to collectively as "aromagnetism." These properties have been found in experiments on suspension of these crystals in water and other liquids (concentrated or dilute  $H_2SO_4$ ,  $D_2O$ ,  $CCl_4$ ,  $HCl$ , and  $KOH$  or high-purity mineral oil). These properties are the same in all the disperse media listed here.

We studied suspensions of microscopic crystals of these substances in very low concentrations. When these small crystals (always aspherical) are oriented, a (double scattering)-(di-Tyndallism)-(conservative dichroism) (Planck's terminology) arises. The extent to which polarized light beam is attenuated depends on whether the polarization is directed along the orientation or perpendicular to it. At a fixed polarization, a periodic change in the orientation axes of the particles (in the case at hand, in a magnetic field) causes a periodic modulation of the light displayed on an oscilloscope.

When sign-varying square magnetic field pulses are imposed on a suspension, a light modulation wave is excited. The excitation begins at the time at which the field changes sign, and it decays toward the end of the pulse. Since the observed reorientation could result from only a constant magnetic moment  $\mu$  of the particles, the existence of such a moment is proved.

We recall that the orientation of the particles associated with the anisotropy of the magnetic polarizability is an effect which is quadratic in the field  $H$  (one power of  $H$  induces a moment in a tensor fashion, and the second power of  $H$  rotates this moment along with the particle). This field  $H$  is a field in which we have  $H^2 = \text{const}$ . It could not cause a reorientation of the particles, and there could be no modulation of light. The fact that there is a modulation proves that there exist small crystals with a magnetic moment  $\mu m$ . Control experiments with small crystals not exhibiting an aromagnetism demonstrate that there is no modulation.

If a suspension is placed in a rotating field with a constant magnitude  $H$  and a small rotation frequency  $\omega$ , the small crystals rotate with the field. The resultant

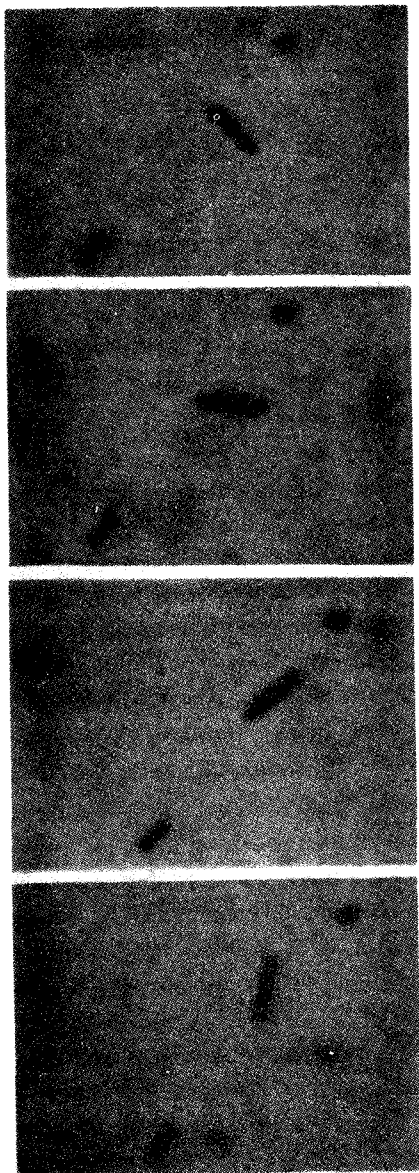


FIG. 1. Photomicrographs of a small pyrene crystal. The aromatic crystal rotates upon an instantaneous reversal of the magnetic field. *a*—The long axis of the crystal is oriented along the field; *b-d*—successive positions of the crystal after the reversal of the magnetic field (the two fixed images on these micrographs are small crystals which have settled on the bottom of the vessel and have become attached there).

orientation axis also rotates, and polarized light is modulated at a frequency of  $2\omega$ . Because of friction, the resultant orientation axis lags an angle  $\alpha$  behind the field  $H$ . Experiments show that  $\alpha$  remains constant if there are proportionate increases in  $\omega$  and  $H$ . Since the moment of friction is proportional to  $\omega$ , the torque caused by  $H$  is also proportional to  $\omega$ . The small crystals following the field thus have a magnetic moment  $\mu$  which is constant, independent of  $H$ ; otherwise, we would find  $\alpha = \text{const}$  at  $\omega/H = \text{const}$ .

The substances of which the small crystals in the present experiments were made are known to be excellent dielectrics and ordinary anisotropic diamagnets. We found that the latter comment is true only in fields  $H > (3-5) \times 10^3$  Oe, at which the normal anisotropic magnetic polarizability proportional to  $H$  comes into play, but when it begins to outweigh the constant  $\mu$ , the torque becomes proportional to  $H^2$ , and the measurements reveal  $\alpha = \text{const}$  at  $\omega/H^2 = \text{const}$  in these strong fields. The results of our measurements agree with tabulated data in the literature on the anisotropy of the magnetism. Our measurements in fields  $H \leq (3-5) \times 10^3$  Oe, in contrast, yield a completely different picture: A significant fraction of the small crystals have a *constant* magnetic moment  $\mu$ , which is proportional to the volume of the small crystals (as was verified by varying the volume over five orders of magnitude). Those particles of a given ensemble which do not have a  $\mu$  exhibit an anomalously large anisotropic-magnetic nonlinear polarizability, and the induced moment essentially reaches saturation even in weak fields  $H$ . For those of the small crystals which are sufficiently large (e.g., 300  $\mu\text{m}$  long in the case of a rod),  $\mu$  reaches  $2 \times 10^8 M_B$ . The constant magnetic moment per aromatic molecule is  $1.8 \times 10^{-4} M_B$ . This value is approximately the same for all the substances which we listed at the beginning of this letter. The vector  $\vec{\mu}$  of a small crystal is directed in such a way that it becomes oriented in an external field  $H \leq (3-5) \times 10^3$  Oe in the same way as at  $H \geq (3-5) \times 10^3$  Oe, at which the ordinary diamagnetic anisotropy becomes the dominant orienting factor. The average direction of  $\vec{\mu}$  is therefore perpendicular to the average direction of the normals to the planes of the benzene rings of the molecules.

That there is a constant  $\mu$ , even for the larger of the small crystals, which are clearly visible under a microscope, follows directly from the photographs in Fig. 1: The reorientation of a small crystal upon a reversal of the field occurs through nearly  $180^\circ$  can be seen clearly, since the rotation of a long crystal takes 5–20 s. The induced torque (which is quadratic in the field  $H$ ) obviously could not rotate  $180^\circ$ .

Certain of these substances (pyrene and phenanthrene) undergo a phase transition, at  $69^\circ\text{C}$  and  $97^\circ\text{C}$ , respectively, as we learned. The axis of the diamagnetic anisotropy and the  $\mu$  axis rotate simultaneously through  $\pi/2$  with respect to the crystal habit. This process can be reversible. We established solidly that there was no ferromagnetic contamination of these small crystals, particularly in the form of ferromagnetic domains. A small crystal 1–2  $\mu\text{m}$  in size has an orientation energy  $\gtrsim kT$  in the geomagnetic field.

All the aromatic substances which we studied are excellent dielectrics with a molecular lattice. There are no free electrons. The molecules are anisotropically diamagnetic; the overall diamagnetism is large; and the molecules of these substances do not have a spin and thus could not be paramagnetic. Nevertheless, the small crystals of

these substances are permanent magnets with an extremely stable magnetism, as we have seen. This stable magnetism cannot be explained by the standard theory of spin magnetism.