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1992 J. Phys.: Condens. Matter 4 L567

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## LETTER TO THE EDITOR

# Dielectric constants and the oxide additivity rule—comments on a recent investigation of $\text{MgAl}_2\text{O}_4$ spinel

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Received 13 July 1992, in final form 17 August 1992

**Abstract.** The concept of the additivity of molecular polarizabilities has been shown to provide a powerful means of rationalizing experimental measurements of the dielectric constants of oxides and of recognizing anomalous data. It is pointed out that the deviant behaviour of  $\text{MgAl}_2\text{O}_4$  spinel at room temperature is readily accounted for by an imbalance in the anti-ferroelectric arrangement of permanent dipole moments which arise naturally from its crystal structure. At higher temperatures the dipole moment per octahedral site, calculated to be  $7.56 \times 10^{-31}$  C m, may give rise to a much larger dielectric effect if these dipoles arise through a mechanism similar to that operating in the isomorph  $\text{MnFe}_2\text{O}_4$ .

Measurements of the relative permittivity of solid dielectric substances at low frequency are well known on the one hand for their great sensitivity and on the other for their unfortunate susceptibility to extraneous effects arising from impurities or other unwanted imperfections in the sample under investigation. Consequently, experimental work aimed at achieving theoretical understanding has tended to be focused on the simplest crystalline solids such as the alkali halides. The lack of an adequate microscopic theory, however, is also generally acknowledged (see, for example, Goodman 1980, Rosenberg 1978).

Recently, some useful progress has been made in the compilation of experimental data from oxides by insisting on precision measurements from single-crystal samples of high purity and cubic symmetry (Shannon 1990). Data from non-cubic crystals were only included if the dielectric anisotropy was known. Conversely, where materials were known to be ionic conductors, ferroelectrics or polycrystalline samples the dielectric data were excluded.

Subsequently, further checks on the internal consistency of the oxide data set have been made (Shannon and Subramanian 1989, Subramanian and Shannon 1989, Shannon *et al* 1990, 1991) by testing against the concept of the additivity of molecular polarizabilities as in, for example,

$$\alpha_D(\text{M}_2\text{M}'\text{O}_4) = \alpha_D(\text{M}'\text{O}) + \alpha_D(\text{M}_2\text{O}_3). \quad (1)$$

For this purpose it was assumed that the polarizability,  $\alpha_D$ , could be derived from the measured dielectric constants,  $\epsilon_r'$ , through the Clausius–Mossotti equation

$$\alpha_D = 3\epsilon_0 \left( V_m \frac{\epsilon_r' - 1}{\epsilon_r' + 2} \right) \quad (2)$$

where  $V_m$  is the volume per molecule and  $\epsilon_r'$ , the real part of the complex dielectric constant, is measured in the range 1 kHz–10 MHz. This work has shown that, despite the well known theoretical limitations of equation (2) (e.g. its dependence on the applicability of the Lorentz field), the difference between the two sides of equation (1) is typically no more than 0.5–1% for a remarkably extensive series of aluminates, beryllates, borates, gallates, silicates and phosphates. Deviations greater than this could usually be traced to ionic or electronic conductivity or to the presence of impurities or other defects.

MgAl<sub>2</sub>O<sub>4</sub> spinel is exceptional, however, according to Shannon and Rossman (1991). In this case, careful examination of a wide range of single-crystal samples from various sources showed that the polarizability of the compound is invariably from 1.1–3.2% larger than the sum of the polarizabilities of the oxides MgO and Al<sub>2</sub>O<sub>3</sub>, i.e. the polarizability of spinel is persistently outside the range of behaviour exhibited by most oxide compounds. It is further to be noted that ionic and electronic conductivity and piezoelectricity were eliminated as possible explanations for the discrepancy through the use of auxiliary tests and that effects from cation disorder were also ruled out. However, the presence of permanent dipole moments, a natural consequence of the crystal structure of spinel, does not appear to have been recognized. It is the purpose of this communication to draw attention to the existence of these crystallographic features and to suggest means of revealing their presence more directly.

It is perhaps worth emphasizing in this context that the experimental results obtained by Shannon and Rossman are consistent with previously reported measurements for low-frequency dielectric constant (Wang and Zanzucchi 1971) although the latter were less precise, and also with the known high-frequency (optical) behaviour and with the Lyddane–Sachs–Teller relation (Grimes *et al* 1978). The really new development due to Shannon is the revelation, through experimental precision and comparison of such experimental results from a large number of oxides, that the low-frequency dielectric constant of MgAl<sub>2</sub>O<sub>4</sub> is surprisingly high.

Large values for the low-frequency dielectric constant of ferrites crystallizing with the spinel structure was first noted many years ago (Blechsmidt 1938, Polder 1950) and ferroelectricity was suspected. But an explanation along these lines, as pointed out by Fairweather *et al* (1952), is excluded if the crystal structure is assumed to conform with the conventional centrosymmetrical space group  $Fd\bar{3}m$ . The problem was resolved through the realization that the crystal structure of spinel should properly be referred to the non-centrosymmetrical space group  $F\bar{4}3m$  (Grimes 1971, 1972, Collyer *et al* 1988)—this leads to an anti-ferroelectric arrangement of permanent dipole moments (Grimes 1973).

In the case of MgAl<sub>2</sub>O<sub>4</sub> spinel a high-resolution single-crystal x-ray diffraction study has confirmed that the space group  $F\bar{4}3m$  provides a significantly superior fit to the experimental data (Grimes *et al* 1983). The deviation from the conventionally accepted centrosymmetrical structure arises primarily from oxygen-ion displacements and if the new locations for these ions and for the Al<sup>3+</sup> ions are used as a basis

for calculation the corresponding dipole moment is found to be  $7.56 \times 10^{-31}$  C m per octahedral site, assuming that the cation distribution is normal. In fact a 12% cation inversion was found by Grimes *et al* so the anti-ferroelectric array of dipole moments is likely to be unbalanced. Contrary to the conclusion of Shannon and Rossman, therefore, it is suggested that the cation distribution in spinel could be a primary cause for producing deviations from the oxide additivity rule.

More generally, as the spinel unit cell contains 16 octahedral sites in a volume of  $530 \times 10^{-30}$  m<sup>3</sup>, it is easily seen that the saturation polarization could be as large as

$$P_s = 2.28 \times 10^{-2} \text{ C m}^{-2}$$

if every dipole moment contributes its full effect. Such a circumstance would normally be reflected in a large dielectric constant at low frequencies, but the anti-ferroelectric arrangement of the dipole moments at room temperature provides an effective mask. An example of this kind of situation has been seen in the isomorphic ferrite, MnFe<sub>2</sub>O<sub>4</sub>, where it is believed that the octahedrally coordinated metal ions are displaced off-centre by a potential barrier mechanism (Grimes 1972, 1973, 1974). The dielectric constant of this compound also is unremarkable at room temperature. But at 473 K an enormous enhancement is observed (Peters and Standley 1958), an effect that may be readily interpreted if, at this temperature,  $kT$  exceeds the barrier height at the octahedral site.

If the mechanisms operating in MgAl<sub>2</sub>O<sub>4</sub> spinel and in MnFe<sub>2</sub>O<sub>4</sub> are similar, a comparison of their respective saturation polarizations suggests that the low-frequency dielectric constant in spinel could rise with increasing temperature, reaching perhaps as much as 100. Ideally, this needs further investigation. However, the temperature range should probably be higher than was required for MnFe<sub>2</sub>O<sub>4</sub> as the

$$F\bar{4}3m \rightleftharpoons F'd3m$$

phase transition in spinel may not occur below 933 K (Suzuki and Kumazawa 1980).

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