MAGNETOELECTRICS

Is $CdCr_2S_4$ a multiferroic relaxor?

Arising from: J. Hemberger *et al. Nature* 434, 364–367 (2005)

Materials showing simultaneous ferroelectric and magnetic ordering are attracting a great deal of interest because of their unusual physics and potential applications[1]. Hemberger *et al.*[2] have reported relaxor-like dielectric properties and colossal magnetocapacitance (in excess of 500%) for the cubic spinel compound $CdCr_2S_4$ and related isomorphs[3–5], concluding that $CdCr_2S_4$ is a multiferroic relaxor. We argue here, however, that their results might also be explained by a conductive artefact.

The polarization hysteresis loops of Hemberger *et al.*[2] have a shape unlike that seen in ferroelectrics and more like that of a lossy dielectric[6,7], such as the semiconducting thiospinels. The 'remanent' polarization is much larger than the pyroelectric one, whereas switchable polarization must always be smaller than the pyroelectric polarization — which on its own calls the hysteresis results into question. The pyroelectric polarizations of 0.05–0.07 μC cm^{-2} are themselves tiny for any proper ferroelectric, and are consistent with thermally stimulated discharge of space-charge injected during poling[6].

Ab initio calculations[8] preclude soft phonons, and hence proper ferroelectricity. Nor have Raman experiments[9] found soft phonons or a lack of centrosymmetry. Raman results with wavelengths near or below the resonant edge[10] are consistent with local non-centrosymmetry (a necessary, although insufficient, condition for ferroelectricity) — however, this technique is unreliable because nominally forbidden odd-parity longitudinal-optical phonon scattering can be strong even in centric crystals[11] when there is real absorption.

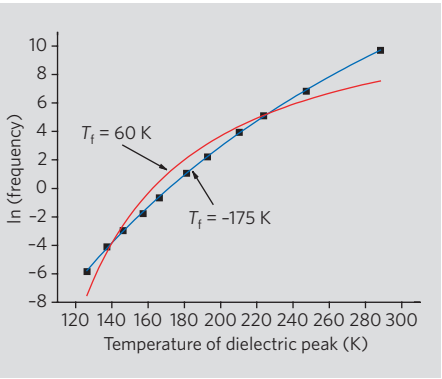

Figure 1 | Temperature of dielectric maxima as a function of alternating-current frequency. Data were extracted from refs 2–4 and fitted with the Vogel–Fulcher law of relaxors. The good fit (blue line) gives a negative value, whereas the T_f (the finite temperature at which the relaxor dynamics 'freezes' into a polarizable state) suggested by Hemberger *et al.*[2] (red line) does not reproduce the data. If T_f is not positive, there can be no remanent polarization. If an Arrhenius law is fitted to the dielectric peaks, the activation energy (about 0.33 eV) (refs 3–5) is similar to that obtained from fitting the conductivity data (0.2–0.3 eV), indicating that the dielectric relaxation is indeed due to the temperature dependence of the conductivity.

Broad dielectric peaks occurring as a function of temperature, and shifting to higher temperatures as the frequency of the alternating current (a.c.) increases, are interpreted by Hemberger *et al.* as evidence that $CdCr_2S_4$ is a relaxor ferroelectric[2]. In a relaxor, the temperature of the dielectric peak (T_m) depends on the a.c. frequency, f, in accordance with the Vogel–Fulcher law: $f = f_0\, e^{-U/k_b(T_m - T_f)}$. Here, T_f is the finite temperature at which the relaxor dynamics 'freeze' into a polarizable state. We have fitted the data for $CdCr_2S_4$ (Fig. 1) and obtain an unrealistic value for T_f of about –175 K. For polarization to be remanent at the temperatures suggested by Hemberger *et al.*, T_f ought to be in the region of 60 K, which does not fit the data (Fig. 1).

Relaxor-like behaviour can actually appear in any heterogeneous semiconductor as a result of the Maxwell–Wagner effect, a conductive artefact unrelated to relaxors[12,13]. The low-frequency divergence of the imaginary permittivity[3–5] is indeed consistent with direct-current (d.c.) conductivity in a Maxwell–Wagner system[13]. Furthermore, any Maxwell–Wagner system (any heterogeneous semiconductor) that is magnetoresistive can show magnetocapacitance[14] (Fig. 2), and the thiospinels are all magnetoresistive[3–5].

Other indicators of magnetocapacitance due to magnetoresistive artefacts[14] are the large effect of magnetic fields on dielectric loss, the strong frequency dependence of the magnetocapacitance and its correlation with magnetoresistance[2–5]. The magnetocapacitance in fact exceeds that possible for linear magnetoelectric coupling[15] and, whereas larger magnetocapacitance is possible for nonlinear coupling, a different temperature and field dependence would be expected; in the thiospinels it is neither proportional to the magnetization M or M^2, nor correlated with the alleged onset of polarization.

Hemberger *et al.* try to rule out contact artefacts by using different electrodes[3–5], but Maxwell–Wagner does not require contact-related depletion layers. The unusual dielectric features disappear on annealing[4], indicating that there could be a heterogeneous distribution of defects that can be annealed out. The authors' single crystals were grown with chlorine as a transport agent, so chlorine-based impurities are one possibility. The authors themselves acknowledge the possibility of sulphur non-stoichiometry[10], so that is another possible culprit.

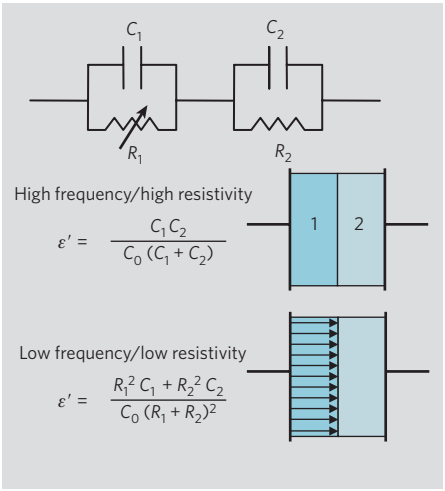

Figure 2 | Maxwell–Wagner equivalent circuit model of a heterogeneous lossy dielectric. The model shows approximated equations for the real part of the apparent dielectric constant (ε') at high and low frequencies of alternating current. At high frequencies, the two types of region act as two capacitors in series (C1 and C2). The effect of lowering the frequency is the same as that of decreasing the resistance (R) of one of the two components: it allows the current (arrows) to flow through, reducing the apparent thickness and increasing the measured capacitance (C). In the thiospinels, applying a magnetic field has the same effect on capacitance as reducing the frequency[2], consistent with negative magnetoresistance in a Maxwell–Wagner system[14].

The greater message here is that magnetocapacitance is not a property of a material, but an impedance measurement of a circuit; it may reflect the intrinsic magnetodielectric properties of the crystal under study[1], or extrinsic parasitic contributions. Artificial magnetoelectric effects are common and do not require that the material be multiferroic. Because these artefacts are more likely in semiconducting samples, such as the spinels, and because all reported data are consistent with a magnetoresistive Maxwell–Wagner effect, this seems to be the most plausible explanation. At a minimum, our analysis shows that evidence for the spinels being true relaxor multiferroics is at present inconclusive.

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Hemberger et al. *reply*

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Catalan and Scott[1] propose an alternative interpretation for our findings[2] for $CdCr_2S_4$ in terms of Maxwell–Wagner effects. They also quote related isomorphs, such as $HgCr_2S_4$ (ref. 3), which has been discussed elsewhere[4,5]. As we have shown, Maxwell–Wagner relaxations can indeed strongly affect the dielectric properties of transition-metal oxides[6,7] and semiconductors[8]. We do not find Catalan and Scott's arguments about $CdCr_2S_4$ convincing, however, and think that our experiments provide ample evidence for multiferroic relaxor behaviour.

Taking the arguments of Catalan and Scott point by point, we explain why we stand by our interpretation. First, lossy dielectrics reveal purely elliptical hysteresis loops. The observed hysteresis is typical for relaxors when saturation is not reached[9]. $CdCr_2S_4$ is not a proper ferroelectric. Because of the history and time dependence of relaxors[9], the thermo-remanent polarization cannot be compared with results from $P(E)$ loops. We excluded space-charge effects by frequency-dependent $P(E)$ measurements[3].

Second, coupled spin and polarization waves, not soft phonons, are the relevant collective excitations in multiferroics[10,11]. Recent Raman experiments[12] revealing local polar distortions cannot be explained by resonance effects: those data were determined with energy that is much larger than the red-shifted temperature-dependent interband excitation. Consequently, the effect of local distortions on the longitudinal-optical intensity is larger than possible resonance contributions. Furthermore, the different temperature dependencies of the longitudinal-optical mode intensities, the absent multiphonon and fluorescent contributions, and small phonon linewidth speak against strong resonance contributions.

In their Fig. 1, Catalan and Scott analyse the peak positions of the temperature-dependent dielectric constant, ε', reported by us[2,13]. Such data do not provide precise information on relaxation dynamics and are hampered by conductivity contributions in semiconducting $CdCr_2S_4$. Figure 1 presents more accurate information on the relaxation rate[13]. At high temperatures, a reasonable description with $T_f \approx 60$ K is possible. An analysis based on $\varepsilon'(T)$, as performed by Catalan and Scott[1], and including the transition regime at low temperatures, leads to an unrealistic value for T_f.

The low-frequency divergence of the loss is a common feature of materials with significant conductivity. The circuit discussed by Catalan and Scott[1] cannot account for the complex behaviour of $CdCr_2S_4$ and more elaborate networks[6,7] would be needed. Magnetoresistance is a necessary but insufficient condition for Maxwell–Wagner-related magnetocapacitance. The field changes the relaxation dynamics[2,13], which explains the effect on the relaxation-related loss and the frequency-dependent magnetocapacitance. The correlation between magnetocapacitance and magnetoresistance arises because both are triggered by the strong field-induced shift of the ferromagnetic transition temperature. Concerning the magnitude of the magnetocapacitance, $CdCr_2S_4$ is not a conventional multiferroic and cannot be treated with the same theoretical footing[2]. The dynamic nature of the effect[2,13] explains the lack of correlation between polarization and magnetocapacitance.

From electron probe microanalysis and the narrow linewidths in X-ray studies using synchrotron radiation, we exclude any non-homogeneous impurity distribution in our single crystals. Meanwhile, we have reproduced all effects in annealed single crystals grown without chlorine and in ceramics doped with indium.

We therefore think that our experiments provide evidence for intrinsic multiferroic behaviour, supporting early assumptions of polar phase transitions and magnetoelectric effects in spinels[14].

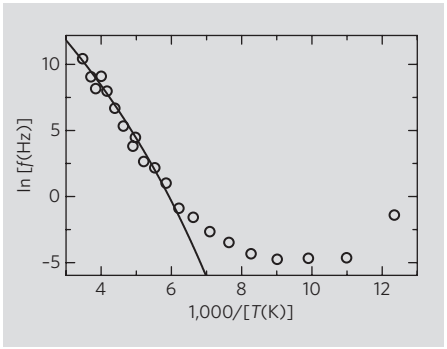

Figure 1 | Temperature dependence of the relaxation rate of $CdCr_2S_4$. The relaxation rate, f, was calculated from the relaxation times τ, shown in ref. 13, determined from fits of the frequency-dependent complex permittivity. These data are more accurate than those analysed in Fig. 1 of ref. 1. As revealed by the Arrhenius representation of Fig. 1, at high temperatures the data follow thermally activated behaviour[13], but they also can be fitted by a Vogel–Fulcher law, with $T_f = 60$ K (line). At low temperatures, strong ferromagnetic fluctuations[2] lead to deviations owing to an acceleration of the relaxation dynamics[2,13].

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