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COMMENT

Glass-like dielectric behaviour of K_2CrO_4

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Abstract. It is shown that results on K_2CrO_4 reported in 1987 by Dissado and Haidar do not invalidate the earlier proposal by Russell and Merlin of the existence of a high-temperature dipole-glass phase.

In a recent Letter, Dissado and Haidar (1987), hereafter referred to as DH, discuss anew the dielectric behaviour of K_2CrO_4 in the vicinity of the α–β transition at $T_c \simeq 940$–60 K (Pistorius 1962, van den Berg and Tuinstra 1978). Their measurements show a strong dependence of the dielectric constants (ε', ε'') on frequency (f), as previously reported by Russell and Merlin (1986), hereafter referred to as RM. Unlike the latter work, however, DH find no evidence of maxima or cusps at temperatures T_f slightly above T_c. RM ascribe the frequency-dependent cusps in the response to the presence of a dipole-glass state mediating the disordered α form and the ordered β phase. DH dispute this interpretation proposing instead that the frequency dispersion is an artefact due to a thin ($\leqslant 10$ Å) 'barrier-layer capacitance'. They further suggest that the maxima are not intrinsic to K_2CrO_4, while indicating that problems with the electrodes used by RM can possibly account for the discrepancies between the two sets of results. I believe that the criticism of the work of RM raised by DH is unwarranted. The different issues are discussed in detail below.

DH believe that the results of RM are inconsistent with glassy behaviour mainly because the f-dependence of ε' persists well above T_f. However, the relevant variable is $|T - T_f|/T_f$ and *not* $|T - T_f|$. The data of RM on K_2CrO_4, plotted as a function of $|T - T_f|/T_f$ and conveniently scaled in frequency, are indeed very similar to those on other dipole-glasses, particularly the systems $KTaO_3$:Li (Höchli 1982) and $(KBr)_{1-x}(KCN)_x$ (Loidl *et al* 1982, Bhattacharya *et al* 1982). The comment by DH that the maxima 'may equally well be due to anomalous behaviour in the relaxation time' associated with the α–β transition is inconsistent with later statements suggesting that the origin of the peaks is extrinsic. In this regard, I recall that the phase change involves an instability at the M point of the Brillouin zone (Sawada *et al* 1976). It is, therefore, unlikely that the anomalies in the dielectric response could result from the α–β transformation.

Does the dielectric response show maxima close to T_c? DH imply that it does not. In particular, they point out the apparent disagreement between the results of RM on ε''

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($f \geqslant 10^4$ Hz) and σ ($=2\pi f\varepsilon''$) data of Natarajan and Secco (1974) at $f = 1$ kHz exhibiting no evidence of maxima. The comparison is, however, misleading. True, there are no clearly resolved peaks near T_c in the experiments of Natajaran and Secco (1974) or those of Miyake *et al* (1981) on the isomorphous compound K_2SO_4, but the measurements of Watanabe *et al* (1973) on K_2SO_4 do reveal well defined cusps. These discrepancies are briefly explained in the work of RM; the expanded argument being that the maxima are difficult to resolve at either too low or too high frequencies. In the former case, as in Natarajan and Secco (1974), the observation of maxima is obscured by the rapidly rising background due to vacancy formation. High frequencies, such as those used by Miyake *et al* (1981), lead to a strong suppression of the amplitude of the peaks leaving only the discontinuity associated with the α–β transition. The sample-dependence of the background and the anisotropic behaviour of the response (the maxima occur only for electric fields parallel to the pseudo-hexagonal axis $\hat{c}$, RM) may futher complicate the finding of the maxima. In this context, it is hardly surprising that the somewhat scanty data of DH, on a poorly characterised sample, fail to reveal the dielectric anomalies. The possibility that the cusps are caused by a malfunction of the Au/Cr electrodes, as hinted by DH who used Pt, can be disregarded; the electrodes in the work of Watanabe *et al* (1973) showing cusps were also Pt.

The claim by DH that the dispersion is due to a 'thin-barrier-layer capacitance' is, for the most part, unsubstantial; proof requires the performing of measurements on samples of varying thicknesses. The data in figure 1 of DH qualitatively support their view, but the dispersion can be as well accounted for by a distribution of Debye relaxations (consistent with the glassy picture). The results in figure 2 of DH on the T-dependence of the capacitance and the conductance add little to the argument. DH note that 'the relaxation time of the dispersion (of ε') possesses the same temperature dependence as the bulk conductance'. But, this is expected in general because of the link (Kramers–Krönig relations) between ε' and ε''. Finally, DH acknowledge the observation of 'electrode interface effects' in their low-frequency measurements. However, it is not clear how these effects are separated from those due to the (supposedly) one monolayer thick capacitance.

In conclusion, the work of DH on K_2CrO_4 does not disprove the observations made by RM. For symmetry reasons, the maxima (or cusps) above T_c in ε' and ε'' (parallel to $\hat{c}$) *cannot* be attributed to the α–β transformation (RM). Parenthetically, I note that *neither* can the pronounced softening of longitudinal-acoustic phonons propagating along $\hat{c}$, as revealed by neutron scattering experiments on K_2SO_4 (Arnold *et al* 1980). These considerations and the $\hat{c}$-correlation suggest that a third (possibly glassy) phase is the source of dielectric and phonon anomalies.

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Reply by L A Dissado and A Haidar

Merlin has raised some points concerning our examination of the dielectric properties of K_2CrO_4 (Dissado and Haidar (1987), hereafter referred to as I). We now reply by clarifying some of the features of our original work.

Firstly our observations and comments were intended to apply only to K_2CrO_4, which we had studied. Although K_2SO_4 is isomorphous with K_2CrO_4, we do not believe that this necessarily means that both must have a dipole-glass intermediate state, and we do not regard the results of Watanabe *et al* (1973) as germane to the present discussion.

Secondly we obtained our data by extensive measurements over six decades in frequency and at twelve different temperatures, made after we had allowed sufficient time for the sample to equilibriate. We think that this is why we were able to observe a discontinuity in the bulk conductance at the transition temperature, which was not found by Natarajan and Secco (1974).

In figure 1, we have replotted some of the results obtained by Russell and Merlin (RM) (1986) so that they may be compared with ours; cf figure 1 of I. It is clear that the replotted data have the same form as the high-frequency tail in the response that we observed. These results, together with the increase in capacitance at 10^4 Hz of about 7 : 1 that we observed between 773 and 900 K (see figure 2 of I), indicate that we have measured the same response with the electric field vector parallel to the pseudo-hexagonal axis. Almost zero change can be expected if the electric field is perpendicular, as RM have shown (see figure 2 of RM 1986).

The asymptotic high-frequency permittivity, for frequencies greater than MHz, in the data of RM appears to be insensitive to temperature as in our data, where we could measure it. The change in ε' and ε'' including the maxima above 1000 K cannot be ascribed to a magnitude change in ε', but rather to a change in the relaxation frequency of the dispersion, as we have shown in figure 1(*b*). In this plot the individual responses have been brought into coincidence by translations along the frequency axis only.

To further characterise the nature of the dispersion, it is essential to carry out measurements at lower frequencies, as we have done (see figure 1 of I). The response observed shows no evidence for a distribution of relaxation times and covers six orders of magnitude in both frequency and capacitance. The latter may be regarded as remarkable for a ferroelectric, let alone for a parallel addition of Debye responses (with equal relaxation times) suggested by Merlin as representing a dipole glass. Merlin is correct when he says that the Kramers—Kronig relationship would lead to the same activation energies for the real and imaginary components of permittivity of a single response; but this is not likely to be true when a bulk conductance acts in parallel with the dielectric dispersion. It was to eliminate precisely this possibility that the point was made. Since the AC conductance has the same activation energy as that measured by Natarajan and Secco (1974), which was attributed to a bulk transport process, we believe that it is a