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High-temperature dielectric properties of ruby mica perpendicular to the cleavage planes

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Measurements of the dielectric properties of mica normal to the cleavage planes with platinum, silver and graphite electrodes are reported, we believe for the first time in the frequency range 0.01 to 10 000 Hz at fixed temperatures in the range up to 956 K. At high temperatures and low frequencies volume transport is observed giving rise to electrode-independent low frequency dispersion (LFD) in which both the real and imaginary components of the complex permittivity vary nearly inversely with frequency. This differs from conventional direct current transport in that a large amount of charge is stored in the system. The activation energy is approximately 2 eV. This is followed at higher frequencies by a volume loss peak which is associated with imperfections in the mica. At still higher frequencies and lower temperatures a loss peak appears, with a high-frequency power-law dependence with an exponent of approximately −0.3 to −0.6, depending on the nature of the electrodes. This is interpreted as a projection to higher frequencies of an electrode-related polarisation process in series with the low-loss interior of the mica sample.

1. Introduction

Micas represent a class of minerals consisting of silicates of aluminium with varying admixtures of potassium, magnesium, iron, chromium and others, but not typically of calcium. They are all characterized by plate-like morphology and perfect basal plane cleavage. Our results relate to muscovite mica of the chemical composition $H_2K \cdot Al_3(SiO_4)_3$. The structure of mica makes ionic motions normal to the cleavage planes very difficult and the same is true of electronic transport, so that micas are excellent insulators with a considerable resistance to thermal decomposition. Micas contain small amounts, 4 to 6%, of water which are given off on strong heating between 500 and 1000° C [1, 2].

As naturally occurring minerals micas contain various additives and imperfections and, in particular, they may be coloured due to the presence of some ionic species and they may also contain inclusions of gaseous, liquid or solid matter. Depending on their purity, the dielectric loss angle δ may vary between 10^{-4} and 0.1 radians [3, 4].

Despite their widespread use in electrical insulation for many years, the dielectric properties of mica are not well documented in the literature, particularly since most of the data are given in the form of graphs of $\tan\delta$ against temperature at constant frequencies, and this form of representation is inherently less informative than the frequency dependence at constant temperatures [5].

The present paper is concerned with the measurement of the dielectric properties of ruby mica samples with a variety of metallic electrodes and we report, we believe for the first time, data for the frequency range 10^{-2} to 10^4 Hz at fixed temperatures between 300 and 956 K. Both our frequency and temperature ranges are wider than those previously reported in the literature. The corresponding dielectric properties of ruby mica along the cleavage planes were reported elsewhere [6], as were also the properties of mica paper [7].

2. Experimental details

Our samples were cleaved directly from sheets of mica and were then cut to approximately 20 × 20 mm^2 size, their thickness varying between 0.02 and 0.4 mm. The electrodes were placed in the centre of the samples and had a diameter of approximately 10 mm. Aluminium or gold were evaporated on some samples, alternatively silver or platinum paint were used. The sample holder consisted of a silica tube with two silica rods running down its length and carrying fine platinum wires with platinum plate electrodes at the bottom, where a platform was provided for positioning the samples between the plate electrodes. The samples were held by a central rod which was spring loaded at the top to provide pressure contacts to the sample.

The whole assembly was placed in a non-inductively wound furnace capable of reaching a temperature of 1200 K and the sample temperature was measured by a chromel–alumel thermocouple attached to the sample holder. The other junction was kept in an ice point unit and the thermo-e.m.f. was monitored by a digital voltmeter.

Dielectric measurements were performed on a Solartron frequency response analyser (FRA) specially adapted for this purpose in our laboratory [8, 9] and

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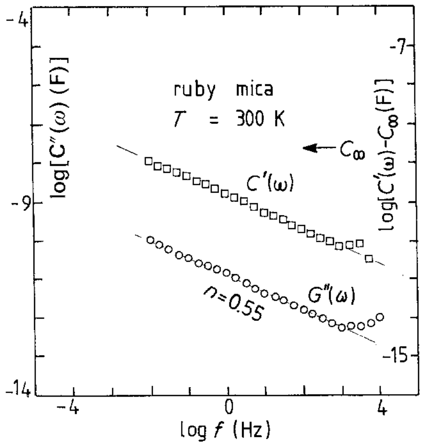

Figure 1 The real and imaginary components of the complex dielectric susceptibility of ruby mica at 300 K, plotted in logarithmic coordinates against frequency. The position of C_∞ is indicated. The real part is raised by two decades with respect to the imaginary part to avoid confusion – the value of the exponent $n = 0.55$ corresponds to the ratio $\cot(n\pi/2) = 1.18$ in which on our logarithmic plot means virtual overlap. The rise in values at the high-frequency end is probably an artefact.

capable of covering the range 10^{-4} to 10^4 Hz in an automated computer-controlled manner. For reasons of economy of time, the lowest two decades of this range were seldom used. The apparatus has a $\tan\delta$ sensitivity of the order of 100 μradians.

Some data at frequencies above 100 Hz were checked on a high-precision General Radio 1620 System and they were found to be in good agreement with the FRA data.

3. Results and discussion

We present our dielectric data in the usual mode of logarithmic plots of the real and imaginary components of the complex frequency dependent capacitance $\tilde{C}(\omega) = C'(\omega) - iC''(\omega)$, the imaginary part being related to the alternating current (a.c.) conductance $G(\omega) = \omega C''(\omega)$, where $\omega = 2\pi f$ is the angular frequency and f is the circular frequency in Hz. Where appropriate we plot alternatively the real part of the "susceptibility" $X'(\omega) = C'(\omega) - C_\infty$ where C_∞ is the high-frequency limit of C', since this quantity is directly Kramers–Kronig compatible with the imaginary component $X''(\omega) = C''(\omega) - G_0/\omega$ where G_0 is the d.c. conductance, so that self-consistency of the data may be immediately checked by visual inspection.

We begin with the presentation of the data for a sample of mica at 300 K Fig. 1, with evaporated gold electrodes. The data follow the "universal" power law of dielectric relaxation

$$\tilde{X}(\omega) = A_n(i\omega)^{n-1} \tag{1}$$

hence

$$X''(\omega)/X'(\omega) = \cot(n\pi/2) \tag{2}$$

where A_n is a constant and the exponent n takes values in the range between 0 and 1. In the present instance $n \cong \frac{1}{2}$, so that the real and imaginary components are almost equal to one another.

The value of C_∞ is indicated on the diagram and $\tan\delta \cong 10^{-3}$ at the upper end of the frequency range, with values approximating to 0.3 at the lower end of the spectrum, suggesting that the mica sample was not of the "best" in terms of what is claimed in the literature.

We found it impossible to obtain an unequivocal value for the loss spectrum at room temperature, and this on account of strong variations between individual samples according to their past treatment. It appears that water adsorbed on the sample may have a significant influence on the loss spectrum. Cycling the temperature between 20 and 100° C did not necessarily produce consistent results either. On looking for the corresponding information in the literature we found that no data were available at low frequencies and near room temperature, so that there was not much to compare our results with. We have chosen the particular example shown in Fig. 1 somewhat arbitrarily, because it exhibited a single power law over the entire available frequency range, with the exception of the upturn at 10 kHz which we believe to be an experimental artefact. In the absence of other information to the contrary we propose to treat the result shown in Fig. 1 as representative of the behaviour of "pure" mica.

Similar uncertainty attaches to the question of the effect of contacts to mica on the measured dielectric loss – it is not possible to make contactless measurements in this frequency range.

Some of the complexities of loss spectra over a range of temperatures are shown in Fig. 2 which relates to a sample with platinum paint electrodes. All our measurements were being taken with increasing temperature, in view of the possibility of irreversible effects arising from the expulsion of moisture from the sample.

The lowest temperature data in Fig. 2 differ significantly from those in Fig. 1, illustrating the difficulty mentioned above. It would appear that a loss peak is superimposed on the power law trend of Fig. 1, and this loss peak moves gradually to higher frequencies with rising temperature, while at the same time the entire shape of the spectrum changes in a manner which makes it impossible to obtain a proper normalization of the data by lateral shifting of the sets corresponding to different temperatures. This suggests quite evidently that changes are taking place in the system which go beyond the normal evolution of a simple loss mechanism with a temperature-dependent loss peak frequency. This is another illustration of the onset of other phenomena.

Between 474 and 716 K we note the development of a second loss peak process which is bounded at the lower frequencies with a strongly dispersive loss behaviour dominating the response at higher temperatures. The slope of this loss deviates significantly from the – 1 value which would be consistent with d.c. conduction, and we shall see in Fig. 3 and others that there is clear evidence of low-frequency dispersion (LFD) which follows the universal law (Equation 1) but with very small values of the exponent n, of the order 0.03 in the present case. The high-frequency end retains a distinctly shallower slope.

The data for the same sample plotted separately for

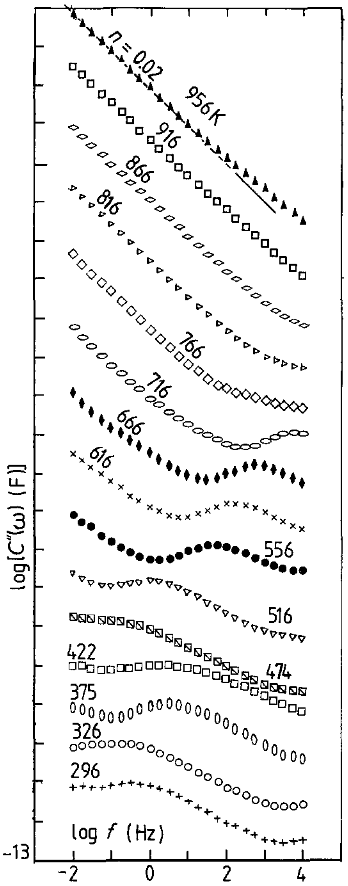

Figure 2 A compilation of loss data for a ruby mica sample with platinum paint electrodes for temperatures in the range 296 to 956 K, with rising temperature during the measurement run. Each successive set is displaced vertically by one decade to avoid overcrowding and to reveal the structure of the spectra. At the highest temperature we show the prevailing slope which is fractionally less than -1, with $n = 0.02$.

$C'(\omega)$ and $C''(\omega)$ on common axes, and therefore hiding much of the detail visible in Fig. 2, are shown in Fig. 3, which also gives the normalization of these data together with the displacement locus of a representative point. It is evident that the shape of the response is changing gradually, making it impossible to obtain a unique "master curve", but the principal features are clear, nevertheless.

Figs 4 to 7 give similar sets of data, respectively, for another sample with platinum paint electrodes, two with silver paint electrodes and one with metal backed graphite electrodes. In all cases normalization becomes possible at temperatures in excess of some 400 to 500 K, and this is the region where the effects of water content would have been eliminated.

Four principal features appear quite clearly in all five sets of data in Figs 3 to 7 and they may be summarized as follows:

(i) a high-frequency, low-temperature response of the type shown in Fig. 1 with the exponent $n \cong \frac{1}{2}$ for graphite and platinum and $n \cong 1/3$ for silver paint. This part is therefore somewhat electrode-dependent.

(ii) region (i) is terminated at lower frequencies by a distinctive loss peak which is particularly well visible in platinum contact samples and less strongly so in silver contacts, the reason in the latter case being probably partly due to the lower slope of the prevailing trend in (i). This region is also electrode-dependent.

(iii) an intermediate-frequency loss peak visible as a dispersion of $C'(\omega)$ because $C''(\omega)$ is dominated by the LFD process. This process appears to be independent of the material of the electrodes.

(iv) a low-frequency, high-temperature LFD region which appears to be independent of the material of the electrodes. The values of the exponent are so small that they are better characterized in terms of the corresponding ratio which defines $\cot(n\pi/2)$ which falls between 30 and 60, with some uncertainty introduced by the overlapping region (iii).

In Figs 5 to 7 the position of the real part of $\tilde{X}(\omega)$ is given by the dotted line in the correct relation to $X''(\omega)$. There is a region of power law dependence of both components of $\tilde{X}(\omega)$ between the loss peak and the onset of LFD but the experimental evidence is insufficient to enable further conclusions to be reached.

The major feature of the response in all cases is the combination of the electrode-dependent regions (i) and (ii) which occur at high frequencies so that they most likely correspond to the bulk response, since they are too weak to be directly attributable to interfacial processes at the electrodes. At the same time, it is very unlikely that electrode material should somehow penetrate into the volume of the samples, particularly at the relatively low temperatures at which these features are clearly visible. Ionic transport at right angles to the cleavage planes in mica appears to be very difficult.

We therefore propose an alternative interpretation based on a "reflection" of an interfacial loss peak on the apparently volume response of the system. For an approximate analysis of this phenomenom, consider the series combination of a lossy capacitor, assumed for simplicity to be of Debye nature given by

$$\tilde{C}(\omega) = \frac{C_0}{1 + i\omega/\omega_p} \tag{3}$$

and of an ideal loss-free capacitor C_0. In our system, C_0 corresponds to the nearly loss-free interior of the mica sample, and $C_\infty \gg C_0$, with ω_p being the loss peak frequency for the interfacial process. The effective capacitance of the combination is then given by the approximate relation

$$\tilde{C}(\omega) \cong \frac{C_\infty}{1 + i\omega/\omega_{p'}} \tag{4}$$

with

$$\omega_{p'} \cong (C_0/C_\infty)\omega_p \tag{5}$$

The series combination appears therefore as a much smaller capacitance, with its loss peak frequency being much higher than the interfacial capacitor in its own right. This model would explain the appearance at high frequencies of a loss process which in fact takes place at much lower frequencies in the electrode/insulator interface.

The exact mechanism of this interfacial loss is not clear at present and we have no independent confirmation of its existence or physical nature, but we suggest that the present dielectric information is

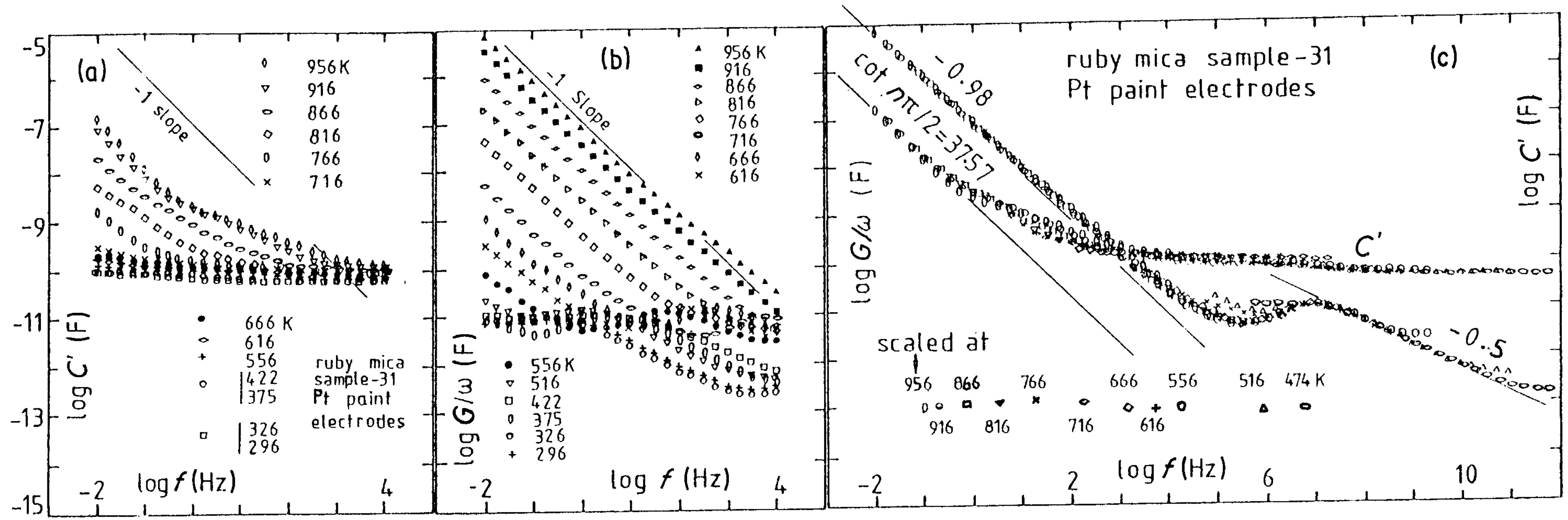

Figure 3 The complete dielectric response of the same samples as in Fig. 2, with platinum paint electrodes, showing separately the real and imaginary components of the complex capacitance and also their normalization into a single master curve. The displacement locus of a representative point is shown and characteristic slopes are drawn in, with Kramers–Kronig compatible positions of the two components shown in the LFD region. The two lines with −1 slopes are drawn in identical positions, for comparison.

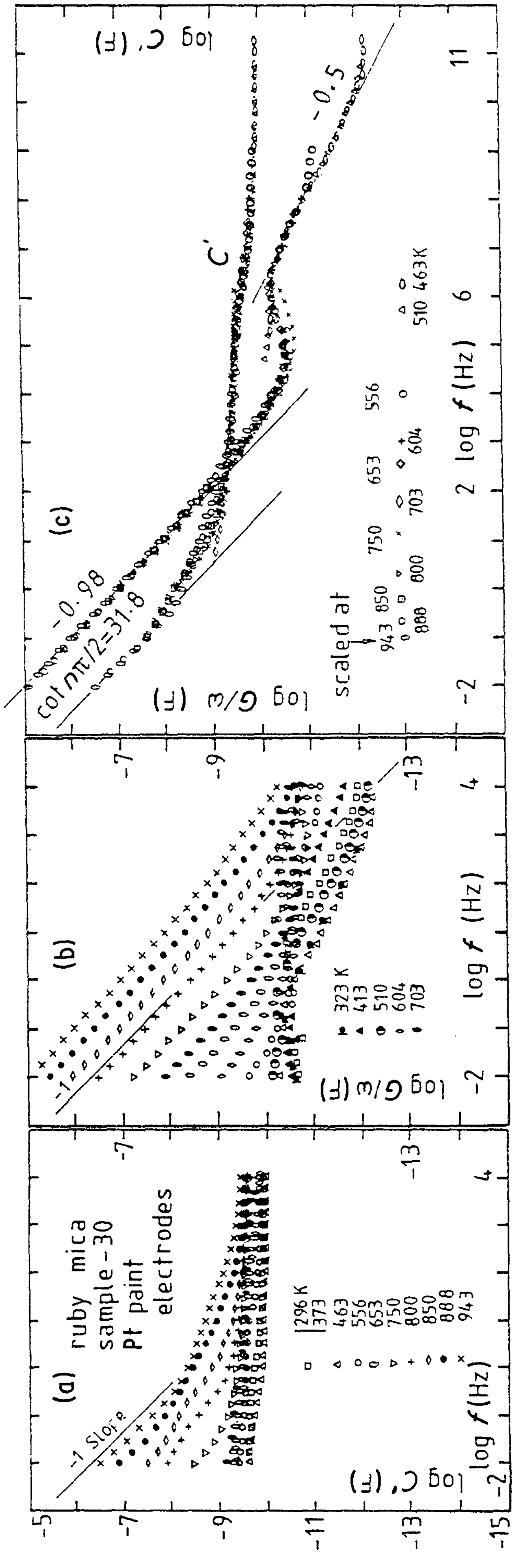

Figure 4 Dielectric data for a different sample of ruby mica with platinum paint electrodes in a similar temperature range to that in Fig. 3.

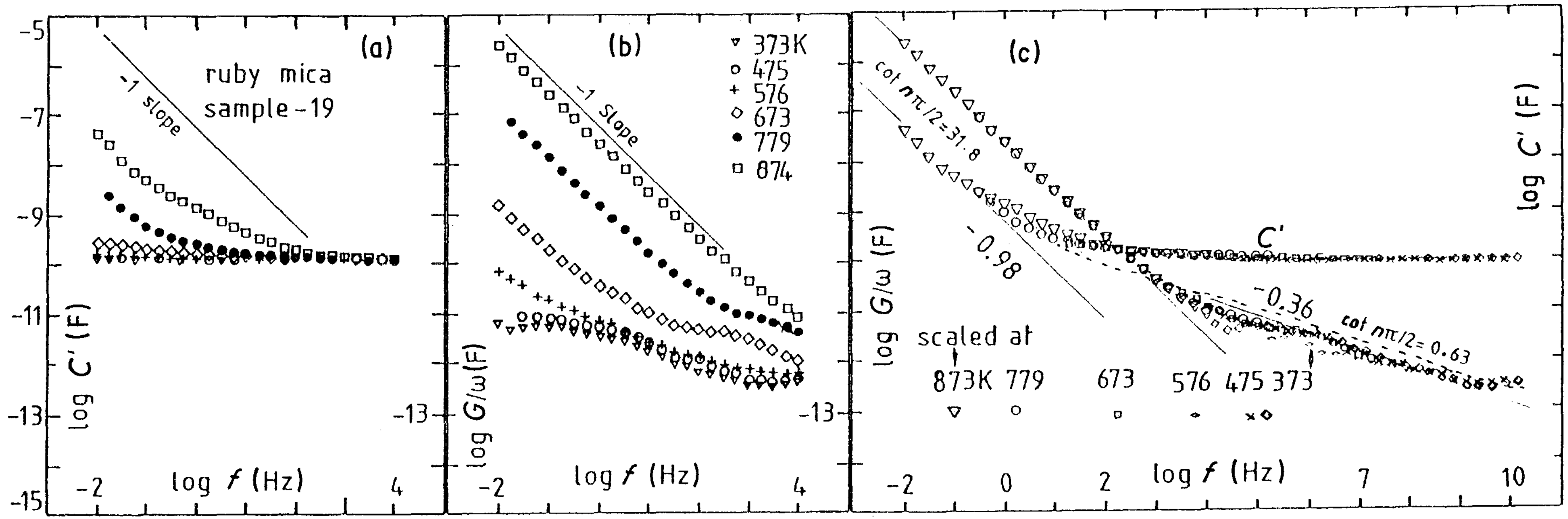

Figure 5 The dielectric response data for ruby mica with silver paint electrodes.

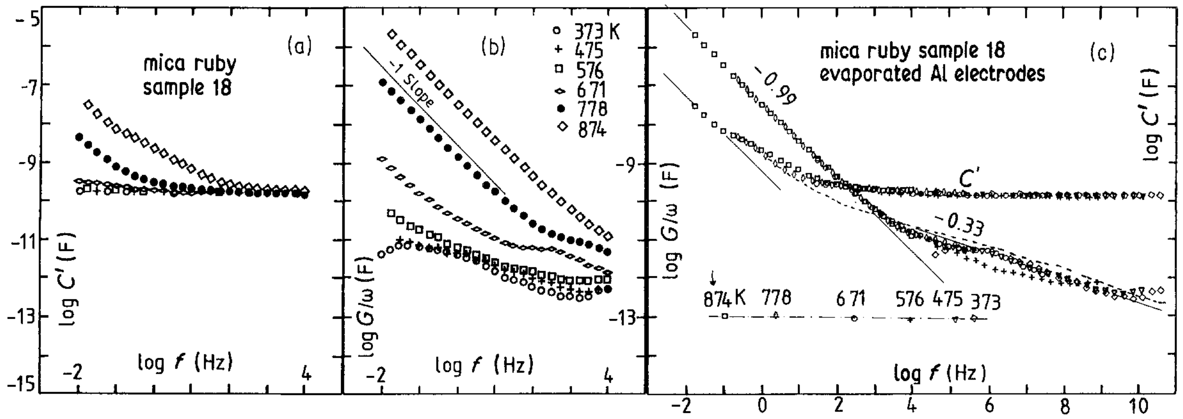

Figure 6 The dielectric response data of a different sample of ruby mica with silver paint electrodes.

unmistakable and should be taken seriously as an incentive for more detailed studies of the mica/metal interface. In order to produce a loss peak these interfacial processes must involve some strictly localized, i.e. dipole-like transitions of electronic or ionic charges across a very thin insulating layer. This could be, for example, the transfer of some metallic ions into the first monolayers of the mica and *vice versa*, but it is unlikely to involve the presence of moisture, since we have independent evidence from our other measurements that these peaks are still present with descending temperatures from 600 K, where all moisture would have been expelled at the beginning.

It should be noted that although the present analysis is based on the assumption of a Debye-like interfacial process, this has been done for the sake of simplicity and the result will be substantially unchanged if the interfacial characteristic is more general in character, so long as a clear loss peak is present.

We now consider the strongly dispersive LFD region at the lowest frequencies and high temperatures which obeys the characteristic Equation 1 with exponent values of the order of 0.02 or so. Since this is the dominant low-frequency process, it must correspond to a mechanism acting in parallel with the bulk capacitance and it cannot in any way correspond to any interfacial process in series with the bulk. This shows clearly that our experimental evidence proves the existence of a volume LFD transport with, in the first approximation, negligible electrode interaction. Since this effect persists unchanged up to temperatures of the order of 900 K, it cannot be due to water-related protonic conduction and we must conclude that it is most likely due to the migration of K^+ ions, which are the only relatively free ions in the system.

This experimental evidence provides one of the few firm examples of volume LFD in single crystalline layer materials like mica. The significance of this conclusion for the understanding of the theoretical basis of LFD will be discussed in the Conclusions section.

This leaves process (iii) which invariably becomes significant as a strong perturbation of the LFD trend (iv) of $C'(\omega)$ approximately one decade above the point where the latter merges into the high-frequency capacitance C_∞. This cannot be due to an interaction between the LFD process and C_∞ since we have concluded that the two must be in parallel with one another, so it must represent an inherent volume transport process. This is further confirmed by the observed apparent lack of correlation with the material of the electrode.

A possible interpretation is in terms of the presence in mica of some inevitable long-range periodicity, defining macroscopic regions of locally higher hopping probability for the K^+ or other ions, compared with interplane hopping elsewhere in the material which gives rise to LFD itself. Such enhanced localized probability could, for example, arise from the presence of lattice defects which perturb the perfection of the impenetrable basal planes of mica.

4. Conclusions

Our measurements on ruby mica, covering wider than previously published ranges of frequency and of temperature and providing, for the first time, frequency scans at constant temperatures, lead to a number of novel conclusions regarding the dielectric behaviour of mica. In particular, we are able to distinguish volume processes which are most noticeable at low frequencies and high temperatures, from interfacial properties which appear at higher frequencies as "projections" of lower-frequency responses.

In the first category, we report the presence of a strongly dispersive LFD behaviour in which both the real and the imaginary components of the complex capacitance follow the same power law in frequency with exponents fractionally smaller than -1. This phenomenon widely observed by us corresponds to "near-d.c. conduction", for which it is generally mistaken by people who do not take the trouble to look in detail at $C'(\omega)$, with the essential difference that a massive charge storage process is involved producing effective capacitance values as high as $10^3 \times C_\infty$ and still not showing any saturation at the lowest frequencies. We believe that our observations on mica constitute the first well-documented example of this type of behaviour in crystalline layer media – most other observations relate to amorphous and glassy media. On the other hand and contrary to commonly accepted notions, we have found no evidence of ordinary d.c. conductivity in our mica samples, even up to the highest temperatures.

The physical processes giving rise to this LFD behaviour, which shows an activation energy of 2 eV, are

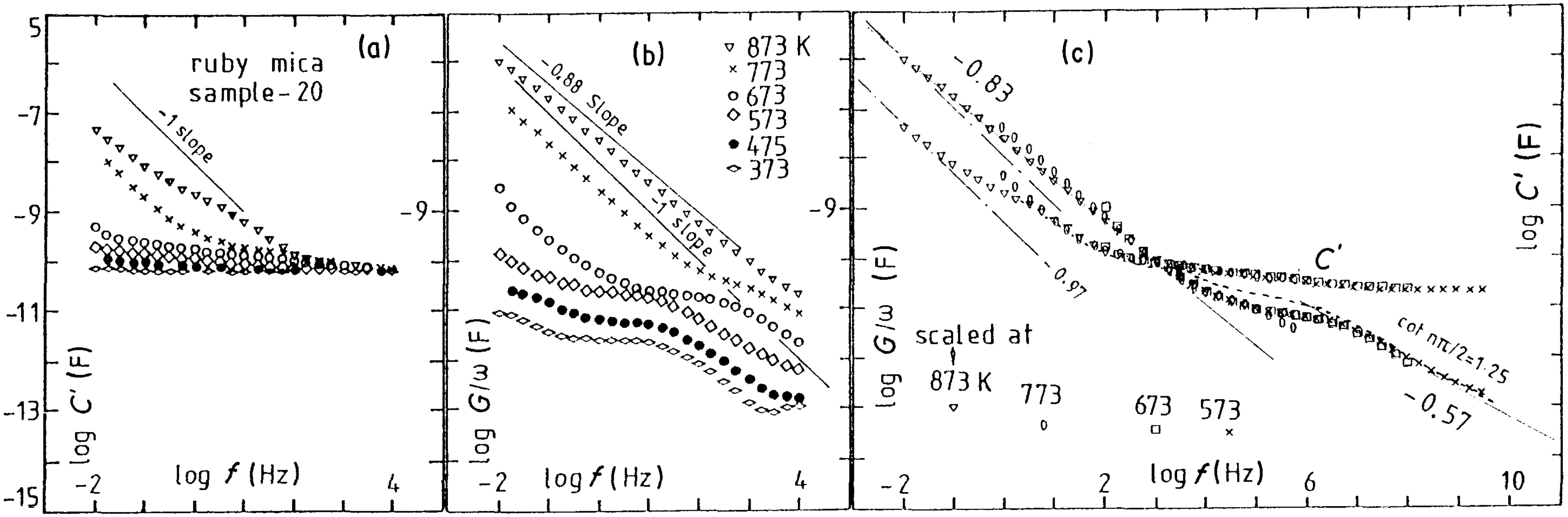

Figure 7 The dielectric response of a sample of ruby mica with graphite electrodes. The two lines with slopes − 1 are in identical positions.

not yet clear, but migration of K^+ ions must be involved over regions which amount to a significant fraction of the thickness of the samples. We cannot say if this results from a spatially uniform migration of individual ions across successive layers of mica or whether some defect-related chain-like motion is involved. It will be interesting to test the applicability of the theoretical treatment by Dissado and Hill [10] and also to explore the possible link of LFD with electrochemical reactions leading to charge storage by means other than electrostatic [11–13].

Our data provide also clear evidence for dipole-like processes related to the electrode materials and which appear at low temperatures and high frequencies. Since material transport from the electrodes into the bulk mica is most unlikely at these relatively low temperatures we suggest that the processes in question are related to the mica/metal interface and become projected into the higher frequency region as a result of a series interaction of this process with the bulk low-loss material. The dipolar nature of these processes must arise from strictly localized charge transitions in the interfacial region.

The widely seen power-law behaviour at high frequencies and low temperatures which underlies other loss processes in this region may be thought to be related to some "diffusive" phenomena which are classically linked with the exponent $n = \frac{1}{2}$. It is worth pointing out that this view is not justified in practice, since we see other values than $\frac{1}{2}$ and since there is no evident physical diffusion process likely to satisfy the stringent conditions attaching to the so-called Warburg mechanism (see [5] p. 305). We suggest that this is a manifestation of the general "universal" many-body relationship and we do not at present understand the reason why these particular values of the exponent should be seen here, which fall mid-way between the low-loss cases of $n \rightarrow 1$ and the LFD where $n \rightarrow 0$.

Altogether, our work shows that the dielectric behaviour of mica is very complex and is little understood in any detail so far. The situation is made more difficult by the fact that highly perfect samples of mica are not readily available and further careful work is necessary to elucidate the properties of this important insulating material.

It is interesting in this connection to note that we were unable to determine the dielectric response of mica at room temperature, where adsorption and desorption of water leads to considerable complications.

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