Analysis of conducting-system frequency response data for an interfacial amorphous phase of copper-core oxide-shell nanocomposites

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Complex electrical-conductivity experimental data sets for the interfacial amorphous phase in copper-core–copper-oxide-shell nanostructured composites have been analyzed using two Kohlrausch-related frequency response models recently developed for analysis of the dispersive electrical response of conductive materials. Such analysis has been carried out for both the precursor (herein referred to as the reference) glass as well as the glass in which the core-shell nanostructure was developed after suitable heat treatment. Complex nonlinear-least-squares data fitting at each temperature employed composite Kohlrausch models that included electrode effects. Because of the lack of sufficient high-frequency data, it was necessary to use fixed, rather than free, values of the shape parameter β_1 of the model. On the basis of topological considerations, its values were set at $1/3$ and $2/3$ for the reference glass and the core-shell structured glass, respectively. The activation energies of resistivity for the reference and the treated glasses were found to have values of about 2 and 0.4 eV, respectively, indicating two different mechanisms of electrical conduction. A blocking-electrode measurement on the reference glass indicated the presence of an electronic as well as an ionic component of the electrical conductivity, with the ionic part dominating at the temperatures for which the present analyses were carried out. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1924541]

I. INTRODUCTION AND BACKGROUND

Recently, Basu, Das, and Chakravorty[1] (BDC) have broken important new ground by comparing the immittance frequency responses at various temperatures of a base silica-gel-derived reference glass (RG) of composition $60CuO \cdot 40SiO_2$, with such a glass first subjected to reduction and then heat treated to produce an amorphous phase of copper-core–copper-oxide-shell nanocomposites (TG). The metallic copper cores have diameters of 3.5–4.8 nm, with a shell thickness varying from 1.0 to 1.6 nm. In the reference sample, the percolative motion of charge carriers takes place in three dimensions, while the motion is likely to be limited to one dimension in the treated material.

Since problems have been identified in the appropriateness of the BDC data analysis method, results of a more suitable fitting method are presented herein. The original BDC approach first involved the estimation from the frequency response data, expressed at the complex modulus immittance level, of the associated distribution of relaxation times (DRT),[2–4] written in the time domain as the sum of 14 Debye response elements.[1] Then the resulting DRT response was itself fitted to a Kohlrausch stretched-exponential expression, not that quoted, which contained a typing error

$$F(t) = \exp(-t/\tau_R)^{\beta}, \tag{1}$$

but the proper form

$$F(t) = \exp[-(t/\tau_R)^{\beta}], \tag{2}$$

where β $(0<\beta\leqslant 1)$ is the stretching parameter and τ_R is the characteristic conductivity relaxation time. Although results were identified as those of dielectric relaxation,[1] for the present conductive system the DRT is that representing resistivity dispersion rather than that of a dipolar-dielectric-dispersive response.

The above analysis approach fitted the modulus data excellently and led to the estimates $\beta \simeq 0.67$ for the RG and ~ 0.47 for the TG material, both virtually temperature independent. But the results of using new data analysis methods[3–10] suggested that these values are unrepresentative of those actually associated only with percolating charge carriers, and thus needed revision. The reason is that the BDC method fits the entire data, data sets that are actually composed not only of bulk percolating response, but also of the effects of the endemic dipolar-dielectric response (represented by a parallel frequency-independent capacitance, the associated undispersed dielectric constant of which is denoted by $\varepsilon_{D\infty}$, and by any electrode effects of significance. It was shown in 1996 that the failure to treat $\varepsilon_{D\infty}$ separately when estimating a conductive-system DRT led to a β estimate that is far different from the true one associated with the percolating process alone.[3] Further, electrode effects are usually present and can distort β estimates even more.[5]

Because of the existence of accurate Kohlrausch frequency response models instantiated in the LEVM computer

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program,[4,6] it is unnecessary to estimate DRT's when fitting frequency response data. There are two such models that follow from the stretched-exponential temporal behavior of Eq. (2); both will be used in the present work. One, the K0 model, is obtained by direct Fourier transformation from time-domain stretched-exponential response.[5,7–10] Note that for conductive systems, $F(t)$ represents the correlation function of the mobile charge carriers. We may write K0 response at the complex modulus level as $M_{K0}(\omega)=M'_{K0}(\omega)+iM''_{K0}(\omega)\equiv i\omega\varepsilon_V I_0(\omega)$, where ε_V is the permittivity of vacuum and $I_0(\omega)$ is the K0 complex resistivity normalized-response function satisfying $I_0(0)=1$ and $I_0(\infty)=0$. We deal with specific quantities so $I_0(\omega)$ involves the parameters ρ_0, τ_o, and β_0, where ρ_0 is the dc value of the complex resistivity, $\rho(\omega)$, τ_o is the characteristic relaxation time of the model, and β_0 is its shape parameter, the β of Eq. (2).

The corresponding response at the complex dielectric constant level, arising entirely from mobile charge, is $\varepsilon_{K0}(\omega)=\varepsilon'_{K0}(\omega)-i\varepsilon''_{K0}(\omega)=1/M_{K0}(\omega)$. Since one finds that $\varepsilon'_{K0}(\infty)=0$, data fitting requires the addition to the K0 response model of a parallel component representing the full high-frequency-limiting dielectric constant, ε_∞. The resulting composite model is designated the CK0.

The second Kohlrausch model, the K1, derived from the K0 model, involves ρ_0, τ_o, and β_1 fitting parameters, where $\beta_1\neq\beta_0$ is the frequency-response shape parameter of the model. K1-model response may be expressed as $M_{K1}(\omega)\equiv i\omega\varepsilon_V I_1(\omega)=[1-I_{01}(\omega)]/\varepsilon_{C1\infty}$, where the 01 subscript indicates that although $I_{01}(\omega)$ is of the form of $I_0(\omega)$, it involves $I_1(\omega)$ fit parameters rather than those obtained by fitting with the K0 model. The important quantity $\varepsilon_{C1\infty}\equiv 1/M_{K1}(\infty)$ is a contribution to the total high-frequency-limiting dielectric constant that is associated entirely with mobile charge effects, and so does not include $\varepsilon_{D\infty}$. Thus $\varepsilon_\infty=\varepsilon_{C1\infty}+\varepsilon_{D\infty}$, and it is necessary that data fitting with the K1 model include a parallel capacitance representing $\varepsilon_{D\infty}$. The resulting composite model is termed the CK1.

No separate fitting parameter is needed to represent $\varepsilon_{C1\infty}$ since it is given by $\sigma_0\langle\tau\rangle_{01}/\varepsilon_V$ for the K1 model. Here $\sigma_0\equiv 1/\rho_0$ and $\langle\tau\rangle_{01}$ is an average over the K0 distribution of relaxation times associated with $I_0(\omega)$ response, a quantity directly estimated from K1-model fitting using the LEVM CNLS fitting program.[3,6–8,10] In the thermally activated situation when Arrhenius response is observed, one usually finds that $T\sigma_0$ and τ_o involve the same activation energy. When this is the case, it follows that $T\varepsilon_{C1\infty}$ is temperature independent, where T is the absolute temperature.[8]

It is noteworthy that since K1 frequency response only follows indirectly from stretched-exponential temporal response, its Fourier transform to the time domain is not of stretched-exponential form. Instead, the equivalent β parameter approaches unity as $t\to 0$ and approaches β_1 only as $t\to\infty$. Extensive CK1-model fitting of frequency response data for homogeneous glasses allowing charge motion in three dimensions has shown that β_1 estimates are very close to $1/3$ and are independent of both temperature and charge-carrier concentration.[8,10,11] Further, topological and other theoretical analyses indicate that, for such glasses involving a single type of charge carrier, the $1/3$ value appears to be universal.[10,11] For $\beta_1=1/3$, it follows that $\varepsilon_{C1\infty}=6\sigma_0\tau_o/\varepsilon_V$. Fits of the same data sets with the CK0 model are usually found to be somewhat inferior to those using the CK1, and the resulting β_0 estimates are larger than β_1 ones and are generally neither temperature nor concentration independent. Both models involve power-law response with an exponent n for $\sigma'(\omega)$, however, when $\omega\gg 1/\tau_o$. Further, fitting of data in this frequency region with both models shows that $n=1-\beta_1=\beta_0$. Thus, fitting data at high relative frequencies with these models leads, for $\beta_1=1/3$, to β_0 and n estimates of $2/3$, a common $\sigma'(\omega)$ log-log slope value found for many different glasses.[10]

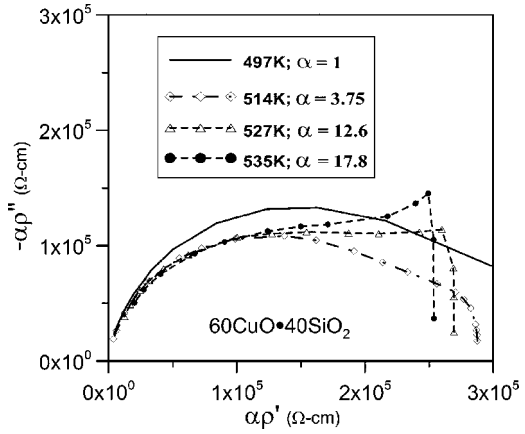

FIG. 1. Scaled complex resistivity plane reference-glass data curves for four different temperatures.

Finally, it is important to emphasize that the K1 response model is the only model that has been derived from both macroscopic[3,12–14] and microscopic analyses.[13–15] Therefore, for fits of the RG material data we shall primarily use the CK1 model, usually with $\beta_1=1/3$ and with added series electrode-effect parameters. For the analyses of the frequency response data of the TG material, the utility of both the CK1 and CK0 models will be investigated. Finally, topological considerations[10,11] suggest that for one-dimensional conduction in microscopically homogeneous regions, $\beta_0=1/3$ and so $\beta_1=2/3$.

II. ANALYSIS OF THE REFERENCE DATA

Before beginning data fitting it is useful to examine the data at different immittance levels. Although plots of both the real and imaginary parts of the modulus response are presented in Ref. 1, they tend to obscure both the high- and low-level responses. A complex plane plot of the data at the complex resistivity level is particularly appropriate for examining low-frequency behavior, while a plot of the real part of the conductivity data, $\sigma'(\omega)$, clearly shows high-frequency bulk and possible electrode response without direct influence from $\varepsilon_{D\infty}$.

Figure 1 presents complex-plane RG resistivity curves for the four temperatures of Ref. 1. In order to compare them all on the same plot, the three higher-temperature data sets have been scaled using the parameter α, the values of which are shown in the legend of the graph. It is clear from these results that the 527- and 535-K data sets exhibit anomalous

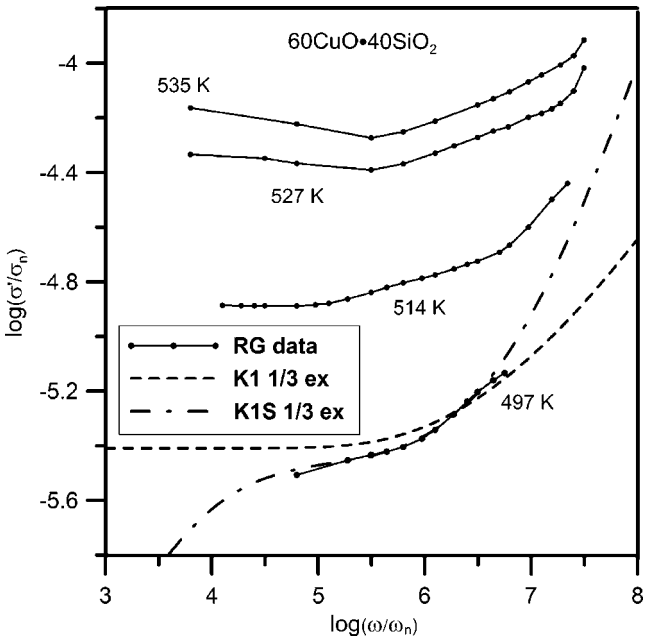

FIG. 2. Log-log plots of $\sigma'(\omega)$ vs ω for the reference-glass data and fit results for the 497-K data. CNLS-fit parameter estimates with β_1 fixed at $1/3$ were used to calculate the separate K1 part of the fit exactly (K1 $1/3$ ex), as well as the response of the full model, including the series electrode part, designated by K1S. Both curves are extrapolated outside of the original data ranges. Here and in Fig. 2 σ_n is 1 S/cm and ω_n is 1 rad/s.

behavior at lower frequencies. It seems likely that the rightmost three points of the 527-K data and the two ones for the 535-K data are in error, are nonphysical, and should be omitted from fitting.

Figure 2 shows log-log plots of the $\sigma'(\omega)$ data for the four RG temperatures. Again the possibly anomalous lower-frequency behavior of the two higher-temperature curves is evident. Further, their highest-frequency values may be outliers as well. In addition to its experimental points, two other responses are presented for the 497-K data set. The one designated K1S $1/3$ ex was calculated from a CNLS fit of the data that included the K1 bulk response model with β_1 fixed at $1/3$ and a series electrode-effect one, given by $\sigma_{SC} \equiv 1/\rho_{SC} \equiv \varepsilon_V A_{SC}(i\omega)^{\gamma_{SC}}$ with $0 \leqslant \gamma_{SC} \leqslant 1$ (yielding complete blocking when $\gamma_{SC}=1$). This model has been termed[5,8,9] the series constant-phase element (SCPE); it involves a power-law exponent of γ_{SC} and leads to a high-frequency-limiting log-log slope of γ_{SC} for $\sigma'(\omega)$. The curve marked K1 $1/3$ ex was calculated from the same fit results, but omitted the ρ_{SC} series contribution. It thus represents the exact K1 bulk response with fitting parameter estimates of ρ_0 and τ_o, as well as the fixed value of $\beta_1=1/3$, leading to a high-frequency-limiting slope of $2/3$.

Since the 497-K data set appears to be the most regular and reasonable of the RG data sets, it was decided to carry out extensive fitting of it using the CK1 model with and without the series ρ_{SC} model. Although both proportional and modulus weighting[6] are used, it is important to note that both choices result in exactly the same CNLS fitting results for data at the $\rho(\omega)$ or at the $M(\omega)$ levels. An important goal of fitting with many different choices is to determine how well a data set can lead to a well-defined estimate of β_1. Therefore, fitting has been carried out with β_1 free to vary and with it fixed at either $1/3$ or $2/3$.

Results of many of the more significant fits carried out are presented in Table I. Note that the parameter values enclosed in square brackets had relative standard deviations from 0.5 up to 100 or more, and are therefore virtually meaningless and indistinguishable from zero. A test of the consistency of data fitted with a given model is to compare fits of all of the data with a smaller set involving only part of the data. In the present situation, we shall use all 12 points of the 497-K data as well as 10-point data that omits the first and last data points.

The four top fit results in Table I involve no ρ_{SC}, and β_1 is taken as a free variable. The large uncertainties of the β_1

TABLE I. CNLS fits of $60CuO \cdot 40SiO_2$ reference glass data at 497 K. N is the number of data points, and P and M denote proportional weighting and modulus weighting. Units of ρ_0 are ohm cm; S_F is the relative standard deviation of a fit; and FQF is a fit quality factor. ( ) denotes fixed parameter values; [ ] indicates those whose relative standard deviation (rsd) estimates are $\geqslant 0.5$, essentially undetermined; { }, those with $0.1 \leqslant \text{rsd} > 0.5$, poorly determined; and #, those with rsd slightly less than 0.1, still not very well determined. All fits were at the modulus level except that of the last row, which is at the complex conductitity level, denoted here by Y. CK1S is the serial combination of the CK1 model and the σ_{SC} electrode-effects SCPE expression.

Model	N/Wt	β_1	$10^{-5}\ \rho_0$	$10^8\ \tau_o$ (s)	$\varepsilon_{D\infty}$	$\varepsilon_{C1\infty}$	$10^5\ A_{SC}$	γ_{SC}	$100S_F$	−FQF
CK1	12/P	{0.191}	3.42	[0.013]	72.5	0.754	⋯	⋯	2.98	89
CK1	12/M	{0.190}	3.33	[0.009]	74.1	0.602	⋯	⋯	2.34	124
CK1	10/P	[0.450]	3.05	[17.3]	{56.8}	16.3	⋯	⋯	1.87	96
CK1	10/M	{0.371}	3.04	[5.50]	{64.7}	8.49	⋯	⋯	1.52	119
CK1	10/P	(2/3)	3.06	135	{11.4}	66.0	⋯	⋯	2.60	83
CK1	10/M	(2/3)	3.02	118	{19.7}	58.7	⋯	⋯	1.93	114
CK1S	10/M	(2/3)	2.49	[59.5]	56.0	35.9	{1.17}	0.66	0.84	141
CK1S	10/M	0.676	2.55	68.3#	51.3#	39.6	(1.81)	0.64	0.90	138
CK1	10/P	(1/3)	3.10	2.94	65.8	6.43	⋯	⋯	1.97	94
CK1	10/M	(1/3)	3.06	2.67	67.4	5.90	⋯	⋯	1.53	120
CK1S	10/M	(1/3)	2.58	{1.40}	82.0	3.96	{1.53}	0.65	0.90	137
CK1S	10/M	0.438	2.57	8.56	76.4	9.92	(1.53)	0.66	0.77	143
CK1S	12/P	0.333	2.82	2.14	73.9	5.14	[1.42]	0.70	2.03	106
CK1S	12/P/Y	{0.331}	2.97	[2.46]	{69.8}	5.90	[1.58]	{0.73}	2.03	106

and τ_0 estimates show that none of these results are significant, even though somewhat better fits were obtained for the $10/P$ and $10/M$ choices, but at the cost of greater parameter uncertainties. The quantities relative standard deviation of a fit (S_F) and fit quality factor (FQF) are different, nonproportional measures of the goodness of a fit. A very good fit occurs when $S_F < 0.01$ and when -FQF is large. The latter quantity depends on the number of data points, the sum of squares of the fit, and the number of free parameters.[6]

Comparison of fit results with β_1 fixed at $2/3$ with those for $1/3$ shows that for the present data better results appear with M weighting than with P weighting, and with 10 data points rather than 12. Further, although better overall fits occur with the inclusion of the ρ_{SC} series model, not all parameters are well defined. With fixed β_1 there is little to choose between the results for $2/3$ and $1/3$! Although the next-to-last row in the table shows results with a β_1 estimate very close to $1/3$, the last row shows that fitting at the complex conductivity (Y) level leads to very poor estimates of several of the free parameters. For data that extend over a wider frequency range with small random errors, fits at the modulus and conductivity levels lead to a very close agreement of free parameter estimates with small relative uncertainties, not observed here.

For data of the present type with a small frequency range and few points per decade, one finds that when β_1 and τ_0 are both taken free to vary their estimated values turn out to be highly correlated, leading to uncertainty in the most appropriate β_1 values, as observed here. Because of this uncertainty, we make the choice of taking fixed $\beta_1 = 1/3$ for all the present RG fits. This is the expected β_1 value for a microscopically homogeneous glass with only one type of mobile charge carrier present.[10,11] Note that the CKIS fit of the fourth row from the bottom, the one shown in Fig. 2, fits the 497-K $\sigma'(\omega)$ data set of that figure very well, but since it did not include the end points of the data, it does not fit them very closely, another instance of the difficulty in obtaining clear-cut results for these RG data.

Perhaps because of the uncertainty in the low-frequency results, as evident in Fig. 1, most consistent ρ_0 and τ_0 versus temperature values were obtained by fitting using the full RG data sets with proportional weighting. For the three lower temperatures full complex-data fitting was used, but estimates of these parameters for the 535-K data set were best with fitting of only the M'' part of the data. Nonlinear least-squares fitting of the resulting values led to an estimate of the activation energy of ρ_0/T of $E_\rho = 2.09 \pm 0.06$ eV and of the E_τ one of 2.14 ± 0.04 eV, overlapping within one standard deviation. Arrhenius fitting of just the ρ_0 values yielded an estimate of 2.05 ± 0.06 eV, in poorer agreement with the above E_τ estimate.

III. ANALYSIS OF THE TREATED DATA

Heat-treated data sets exist for four different temperatures. Unfortunately, they also do not allow well-defined values of β_1 to be estimated from CNLS fitting using the CK1 bulk-dispersion model with additional series parameters to account for electrode effects. Also, fitting with the K0 model fails to yield significant estimates of β_0. Figure 3 shows the $\sigma'(\omega)$ experimental data curves for the four temperatures. All of them, but particularly the three highest-temperature ones, show characteristic responses of just the type produced by electrode effects.[5] It was found that best fitting occurred when the series elements included not only a SCPE, as in the RG data analyses, but also an additional series resistor and a capacitor in parallel with these two elements.

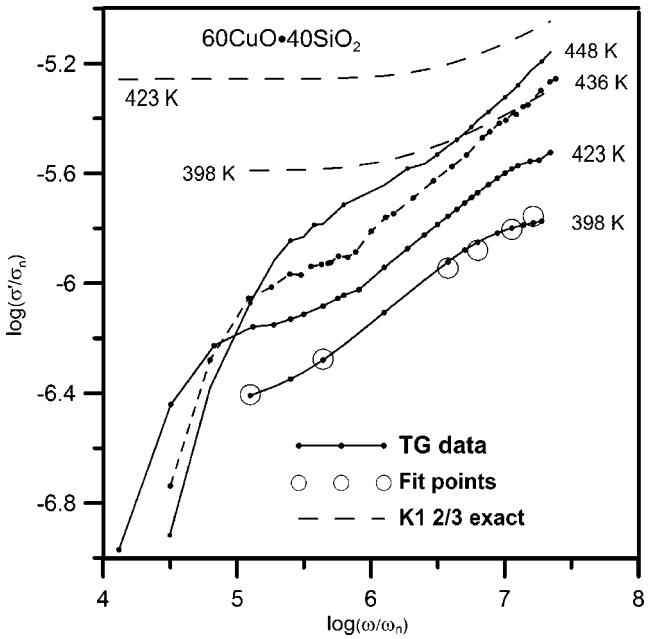

FIG. 3. Log-log plots of $\sigma'(\omega)$ vs ω for the treated-glass data and CNLS $\sigma'(\omega)$ fit results for the 398-K data using the CK1 bulk-response model with β_1 fixed at $2/3$ and an electrode-effects response model in series with it. The two curves designated by K1 $2/3$ exact show the separate K1 responses of the model without series-response contributions.

Although no significant estimates of β_1, with it taken free to vary during fitting, could be obtained, those fits with β_1 fixed at $2/3$ usually led to parameter standard deviations slightly lower than those with β_1 fixed at $1/3$. To the degree that conduction in the nanocomposites of the treated material involves one-dimensional current flow in a microscopically homogeneous material, one would indeed expect[10,11] a β_1 value of $2/3$.

We therefore present here only the results involving this choice of β_1. It was found that with $\varepsilon_{D\infty}$ taken free to vary, fits for the two lowest-temperature values led to reasonably satisfactory values of S_F of about 0.03. Some fit points for the 398-K data set are shown in the figure. In contrast, fits for the two higher temperatures yielded S_F values close to 0.1, quite poor fits. But even worse, as the temperature increased, ρ_0 and τ_0 estimates for the two higher-temperature data sets did not decrease monotonically with respect to those for the lower temperatures.

As mentioned in Sec. I, for the CK1 corrected-modulus-formalism model one expects that $\varepsilon_{C1\infty}$ will be proportional to $1/T$. Therefore, it was decided to use in the fittings those fixed values of $\varepsilon_{D\infty}$ that led to such $\varepsilon_{C1\infty}$ proportionality, yielding $\varepsilon_{D\infty}$ values that themselves showed nearly such Curie-law dependence for the two lower temperatures, but not for the two higher ones. Such fits led to proper mono-

tonic behavior of ρ_0 and τ_o for all but the highest temperature, the results of which suggest either that they were dominated by nonrandom noise or represented the transition to a different conductivity process. Since such results were found only for this one temperature, they cannot be considered to be significant.

Although the CNLS fitting results at the complex conductivity level for the 398-K data were best of all, even they cannot be considered strongly significant. They yielded estimates of ρ_0 and τ_o of about 3.9×10^5 ohm cm and 2.5×10^{-7} s, respectively. First, when the values of the series elements were fixed and fitting of only the $\sigma'(\omega)$ data was carried out, estimates of about $(4.2\pm0.1)\times10^5$ ohm cm and $(1.9\pm0.3)\times10^{-7}$ s were obtained, not much different. But when such real-part fitting was carried out with all the series elements free to vary as well, the results were $(2.0\pm0.05)\times10^5$ ohm cm and $(1.1\pm0.3)\times10^{-8}$ s, quite different indeed.

In spite of these differences, several CNLS fits with different free parameters led to results for the K1-model part of the full response of exactly the forms shown for the two lower temperatures in Fig. 3 and designated by K1 2/3 exact. They show that the K1 part of the full $\sigma'(\omega)$ response is only slightly variable over the present full-frequency range. It is because of such limited variation that no significant estimates of β_1 can be obtained from the present data sets. Simulation indeed shows that the quantity $\sigma'_{\max}(\omega)/\sigma_0$ needs to be of the order of ten or more in order to allow significant estimates of β_1 to be obtained. In the present situation, assuming that $\beta_1=2/3$ so that the limiting high-frequency power-law slope is 1/3, then the data would need to be extended on the high end by at least two or three more decades of frequency.

Estimates of ρ_0 are the most stable and show less dependence on other parameter choices. It is therefore worthwhile to use the CNLS fitting estimates for this quantity, and that of τ_o as well, to carry out Arrhenius fits of ρ_0/T and τ_o for the three lower temperatures. Activation energy estimates were (0.43 ± 0.05) and (0.36 ± 0.05) eV, respectively. For ρ_0, an estimate of (0.40 ± 0.05) eV was found. Although they were associated with mediocre fits, these results are, nevertheless, sufficient to show that the activation energies for the heat-treated material are very different from those of the reference material. They thus suggest that it is likely that the mobile charges for these two situations are quite different, involving perhaps copper ions for the reference material and, as originally suggested in Ref. 1, small polarons for the treated material as where a value of the ρ_0 activation energy of 0.55 was quoted.

In addition, some blocking-electrode measurements carried out on the reference glass at temperatures in the range 497–535 K indicated the presence of significant ionic and electronic conduction. At those temperatures where most of the present data were collected, however, the ionic component dominates the electrical conduction. As a result, a rather high value of activation energy was estimated from this analysis. It should be noted that a high value of resistivity of the reference glass made it impractical for us to make meaningful conductivity measurements at lower temperatures, where the conductivity would likely be dominated by electron hopping.

IV. CONCLUSIONS

Electrical conductivity as a function of frequency was analyzed for a $60CuO\cdot40SiO_2$ gel glass and for the interfacial amorphous phase in copper-core–copper-oxide-shell nanostructured composites using the fitting model of Macdonald based on Kohlrausch frequency response models. The lack of data at high frequencies made it difficult to estimate meaningful values of β_1 by taking it as a free parameter in the complex nonlinear-least-squares analyses.

On topological considerations, β_1 was therefore set at 1/3 for the reference glass and to 2/3 for the treated glass. The activation energies of resistivity for the reference and the treated glasses were estimated to have values of about 2.05 and 0.40 eV, respectively. It is concluded that two different conduction mechanisms are operative in the two glass systems at the temperatures of measurement. The reference glass is believed to have ionic conductivity (involving mobile copper ions) dominating at these temperatures, whereas the treated glass likely has electronic conductivity. Blocking-electrode measurements on the reference glass confirmed the presence of ionic conductivity.

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[1] S. Basu, D. Das, and D. Chakravorty, J. Appl. Phys. **95**, 5741 (2004).
[2] J. R. Macdonald, J. Chem. Phys. **102**, 6241 (1995).
[3] J. R. Macdonald, J. Non-Cryst. Solids **197**, 83 (1996); **212**, 95 (1997).
[4] J. R. Macdonald, J. Comput. Phys. **157**, 280 (2000); Inverse Probl. **16**, 1561 (2000).
[5] J. R. Macdonald, J. Non-Cryst. Solids **307–310**, 913 (2002).
[6] J. R. Macdonald and L. D. Potter, Jr., Solid State Ionics **23**, 61 (1987); The newest WINDOWS version, LEVMW, of the comprehensive LEVM fitting and inversion program may be downloaded at no cost from http://www.physics.unc.edu/~macd/. It includes an extensive manual and executable and full source code. More information about LEVM is provided at this www address.
[7] J. R. Macdonald, J. Appl. Phys. **90**, 153 (2001).
[8] J. R. Macdonald, J. Chem. Phys. **116**, 3401 (2002).
[9] J. R. Macdonald, J. Chem. Phys. **118**, 3258 (2003).
[10] J. R. Macdonald, cond-mat/0403118; J. R. Macdonald, Phys. Rev. B (to be published).
[11] J. R. Macdonald and J. C. Phillips, J. Chem. Phys. **122**. 074510 (2005).
[12] C. T. Moynihan, L. P. Boesch, and N. L. Laberge, Phys. Chem. Glasses **14**, 122 (1973).
[13] J. R. Macdonald, Solid State Ionics **150**, 263 (2002).
[14] J. R. Macdonald, J. Appl. Phys. **95**, 1849 (2004).
[15] H. Scher and M. Lax, Phys. Rev. B **7**, 4491 (1973).