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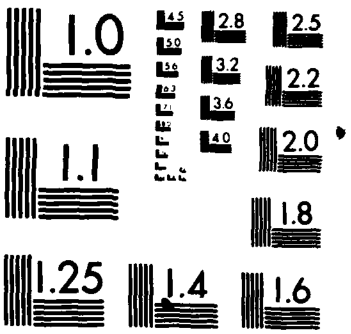

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Electrical Relaxation in Calcium Fluoride Doped with Thorium and Zirconium

by

John J. Fontanella & Mary C. Wintersgill

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Audio frequency electrical relaxation measurements have been performed on CaF$_2$:Th and CaF$_2$:Zr. The nominal concentrations in both cases are 0.1 and 1.0 mol-%. The measurements have been carried out over the temperature range 0.008 to 400K using a fully automated dielectric spectrometer operating at seventeen frequencies from 10 to 100,000 Hz. The spectrum for the 0.1 mol-% thorium doped material consists of three relatively strong relaxations along with two weak relaxations. For the 1.0 mol-% material, the high temperature relaxation, if it exists, is masked by the DC conductivity. Only small changes in the relaxations are noted with a change in the nominal concentration. For 0.1 mol-% CaF$_2$:Zr, seven relaxations are observed all of which appear to be important as significant changes in the spectrum are observed when the nominal concentration is increased to 1.0 mol-%. Models for some of the complexes responsible for the relaxations are presented.

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ELECTRICAL RELAXATION IN CALCIUM FLUORIDE DOPED WITH THORIUM AND ZIRCONIUM*

D.A. Beam, M.C. Wintersgill, J.J. Fontanella
Physics Department
U.S. Naval Academy
Annapolis, MD 21402, USA

D. R. Figueroa
Physics Department
Simon Bolivar University
Caracas, Venezuela

A. V. Chadwick
University Chemical Laboratory
University of Kent at Canterbury
Canterbury, Kent CT2 7NH, UK

C. G. Andeen
Physics Department
Case Western Reserve University
Cleveland, OH 44106, USA

ABSTRACT

Audio frequency electrical relaxation measurements have been performed on CaF_2:Th and CaF_2:Zr. The nominal concentrations in both cases are 0.1 and 1.0 mol-%. The measurements have been carried out over the temperature range 5.5 to 400 K using a fully automated dielectric spectrometer operating at seventeen frequencies from 10 to 100,000 Hz. The spectrum for the 0.1 mol-% thorium doped material consists of two relatively strong relaxations along with three weak relaxations. For the 1.0 mol-% material, the high temperature relaxation, if it exists, is masked by the DC conductivity. Only small changes in the relaxations are noted with a change in the nominal concentration. For 0.1 mol-% CaF_2:Zr, seven relaxations are observed all of which appear to be important as significant changes in the spectrum are observed when the nominal concentration is increased to 1.0 mol-%. Models for some of the complexes responsible for the relaxations are presented.

INTRODUCTION

There has been a great deal of work concerning aliovalent ions in the alkaline earth fluorides.[1] Most of the work has been centered on monovalent and trivalent dopant ions and relatively little information exists concerning tetravalent cations. Consequently, electrical studies of thorium and zirconium in calcium fluoride were undertaken.

EXPERIMENT

Samples of thorium and zirconium doped calcium fluoride were grown using the Stockbarger method.[2] The boules were cleaved and and ground into platelets about 1mm thick. Aluminum electrodes were evaporated onto the faces of the samples in either a two or three terminal configuration.

The temperature control system was fully automated consisting of a Precision Cryogenics CT-14 dewar and LakeShore Cryotronics DRC-82 temperature controller using a silicon diode sensor.

Measurements of the equivalent parallel capacitance, C, and conductance divided by the angular frequency, G/ω, were made at seventeen audio frequencies, 10x, 20x, 31.25x, 50x, and 100x Hz where x=1, 10, 100, and 1000 using a fully automated microprocessor controlled bridge constructed by one of the authors (C.G.A.) which is as sensitive and accurate as the best commercially available manual bridge. As an approximation, the value of ε' at 1000 Hz and 300K was set equal to 6.915 and 7.28 for the 0.1 and 1.0 mol-% samples respectively.[3] The values of ε' at the other frequencies and temperatures were then calculated assuming that the change of ε' with frequency equals that for the capacitance. Finally, values of ε'' at all temperatures were calculated using:

$$\varepsilon'' = \frac{G\varepsilon'}{\omega C} \qquad (1)$$

RESULTS AND DISCUSSION

The results for ε'' vs. T(K) for thorium and zirconium doped calcium fluoride are shown in figures 1 and 2, respectively. Typical plots of ε'' vs. log(f(Hz)) are shown in figure 3. The data were analyzed by estimating the peak positions. The reciprocal of the peak position is taken to be the most probable relaxation time, τ. Typical Arrhenius plots for τ are shown in figure 4. To within the uncertainty, the behavior is Arrhenius, and the best-fit parameters, h and τ_o, in the equation:

$$\tau = \tau_o \, e^{h/kT} \qquad (2)$$

are listed in Table 1.

Thorium doped calcium fluoride

As seen in figure 1, two strong relaxations are observed for thorium doped calcium fluoride. The higher temperature peak occurs at about 357K and 1000 Hz and the strong lower temperature peak occurs at about 71K and 1000 Hz. In addition, three weak features are observed in both the 0.1 and 1.0 mol-% material. The peak just above 40K does not appear to change with concentration and thus may be attributable to a trace impurity. However, that may be fortuitous, since in erbium doped calcium fluoride for example, relaxations occasionally attain a maximum strength at about 0.05 mol-%.[3]

Further work concerning this relaxation is necessary. The other relaxations, those at about 130, 140, and 270K, are extremely weak and will not be considered further.

The presence of a strong, low temperature relaxation (and, in fact, the presence of several weak relaxations) is reminiscent of recent TSDC results for $Ba_{1-x}U_xF_{2+2x}$.[4] Those authors discussed the spectra in terms of (212) clusters composed of two F^- interstitials, a substitutional U^{4+}, and two relaxed lattice fluorine ions. Of course, such a comparison is of limited use since both the host and dopant are different, but to the authors' knowledge, it is the only comparison which can be made for electrical studies of alkaline earth fluorides doped with tetravalent ions. In support of this, there is a significant difference between the results for $Ba_{1-x}U_xF_{2+2x}$ and CaF_2:Th, namely, the presence of a strong, high temperature relaxation in the latter. Coincidentally, a second type of defect cluster has been theoretically predicted for $Ca_{1-x}U_xF_{2+2x}$ by Matar et al.[5] who describe a complex composed of a substitutional U^{4+} ion which is charge compensated by one fluorine vacancy and three fluorine interstitials. Presumably, the reorientation energy for such a complex would be high so that such a complex could be responsible for the high temperature relaxation observed for CaF_2:Th. Whether the reorientation energy is small enough, however, remains to be determined.

Zirconium doped calcium fluoride

As seen in figure 2, the relaxation spectrum for calcium fluoride doped with zirconium is significantly different from that for the thorium doped material. It is, in fact, extremely complex since at least 9 relaxations are involved. The large difference is not unreasonable since there is a large difference between the sizes of Th^{4+} and Zr^{4+}.[6] However, some trends are discernable.

First, the dominant peak (peak 2) is reminiscent of the R_I relaxation in calcium fluoride doped with trivalent ions as the activation enthalpy is 0.4 eV.[7] For calcium fluoride doped with trivalent ions, that relaxation is associated with a substitutional trivalent impurity charge compensated by a nearest neighbour fluorine interstitial. Consequently, at first sight, it might be concluded that the zirconium is trivalent. However, eight other relaxations are observed which makes the spectrum far more complex than for trivalent ions. Further, the dependence with concentration is significantly different. Specifically, as the concentration increases from 0.1 to 1.0 mol-% the 0.4 eV relaxation disappears and peak 3 increases dramatically. At the same time, the remaining peaks also show strong concentration effects. The 1.0 mol-% spectrum has no resemblance with those for calcium fluoride doped with 1.0 mol-% of trivalent ions. Further, since trivalent zirconium ions are not usually observed, it is concluded that zirconium is indeed in tetravalent state and that the 0.4 eV relaxation has a different origin that the 0.4 eV relaxation in rare earth doped calcium fluoride. For example, the peak could be associated with a defect cluster such as the (212) or the trimer mentioned above since both contain a single impurity ion. However, in the event that the same complex is responsible for the strong low temperature relaxation in thorium doped calcium fluoride, the large difference in activation energy would remain to be explained.

Next, the prominent peak (peak 3) in the 1.0 mol-% material is extremely weak in the 0.1 mol-% material and undergoes an extremely rapid increase with concentration at the expense of peak 2. In fact, the increase is faster than linear as an increase in the concentration of a factor of 10 produces almost a factor of 20 increase in peak 3. One possibile origin of peak 3 is a "gettered" complex where potential fluorine interstitials become trapped at a complex. However, the electrical conductivity of the 1.0 mol-% sample of zirconium doped calcium fluoride is extremely low. Of course, it is possible that the "gettered" fluorine ions are strongly bound to the complex. However, the rapid increase of peak 3 at the expense of peak 2 combined with the low electrical conductivity suggest the alternative possibility of a stable complex containing at least two zirconium ions as being responsible for peak 3 in zirconium doped calcium fluoride.

ACKNOWLEDGMENTS

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Table 1. Best fit activation parameters.

Material	Peak	$(\epsilon'_{max})_{approx}$	$\log_{10}\tau_o$	h(eV)
CaF_2:Zr				
0.1 mol-%	2	0.022	-13.7	0.402
	5	0.008	-12.9	0.148
1.0 mol-%	3	0.040	-13.2	0.313
	6	0.005	-12.6	0.116
	8	0.006	-12.5	0.056
CaF_2:Th				
0.1 mol-%	1	0.020	-14.4	0.749
	2	0.035	-12.9	0.131
	3	0.007	-12.4	0.074
1.0 mol-%	2	0.095	-13.0	0.132
	3	0.007	-13.2	0.079

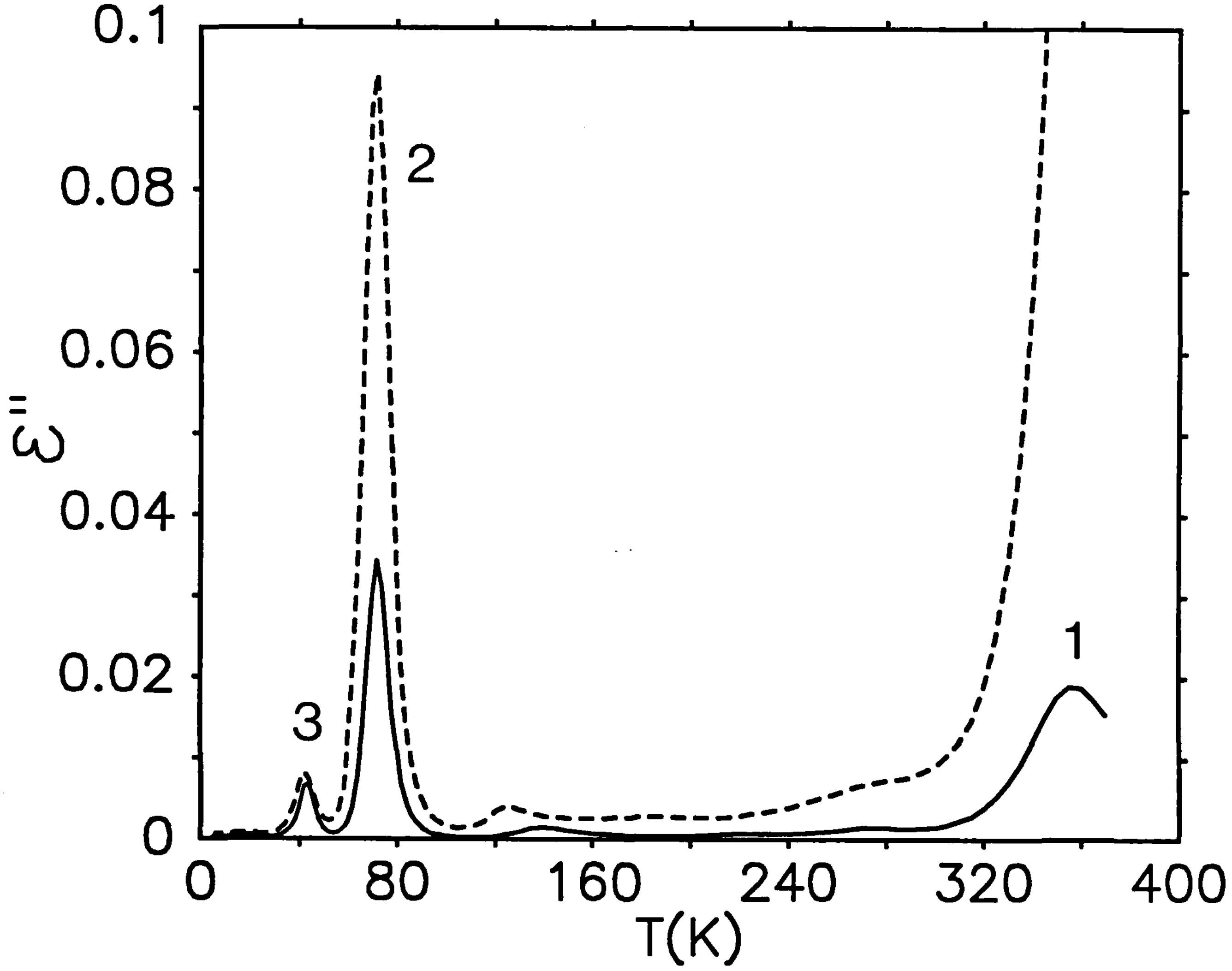
FIGURE CAPTIONS

Figure 1. ε" vs. T(K) at 1000 Hz for calcium fluoride doped with thorium: solid line, 0.1 mol-%; dashed line, 1.0 mol-%. Straight line segments connect the datum points which are not shown.

Figure 2. ε" vs. T(K) at 1000 Hz for calcium fluoride doped with zirconium: solid line, 0.1 mol-%; dashed line, 1.0 mol-%. Straight line segments connect the datum points which are not shown.

Figure 3. ε" vs. Log_{10}(f(Hz)) for calcium fluoride doped with 0.1 mol-% zirconium: triangles (leftmost peak) 184K; squares (center peak) 205.8K; pentagons (rightmost peak) 227.9K.

Figure 4. $\mathrm{Log}_{10}(\tau(s))$ vs. 1000/T (K^{-1}) for calcium fluoride doped with zirconium: triangles (leftmost data) 0.1 mol-% and squares (rightmost data) 1.0 mol-%. The solid lines are the best-fit Arrhenius expression.


0.1
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3
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80
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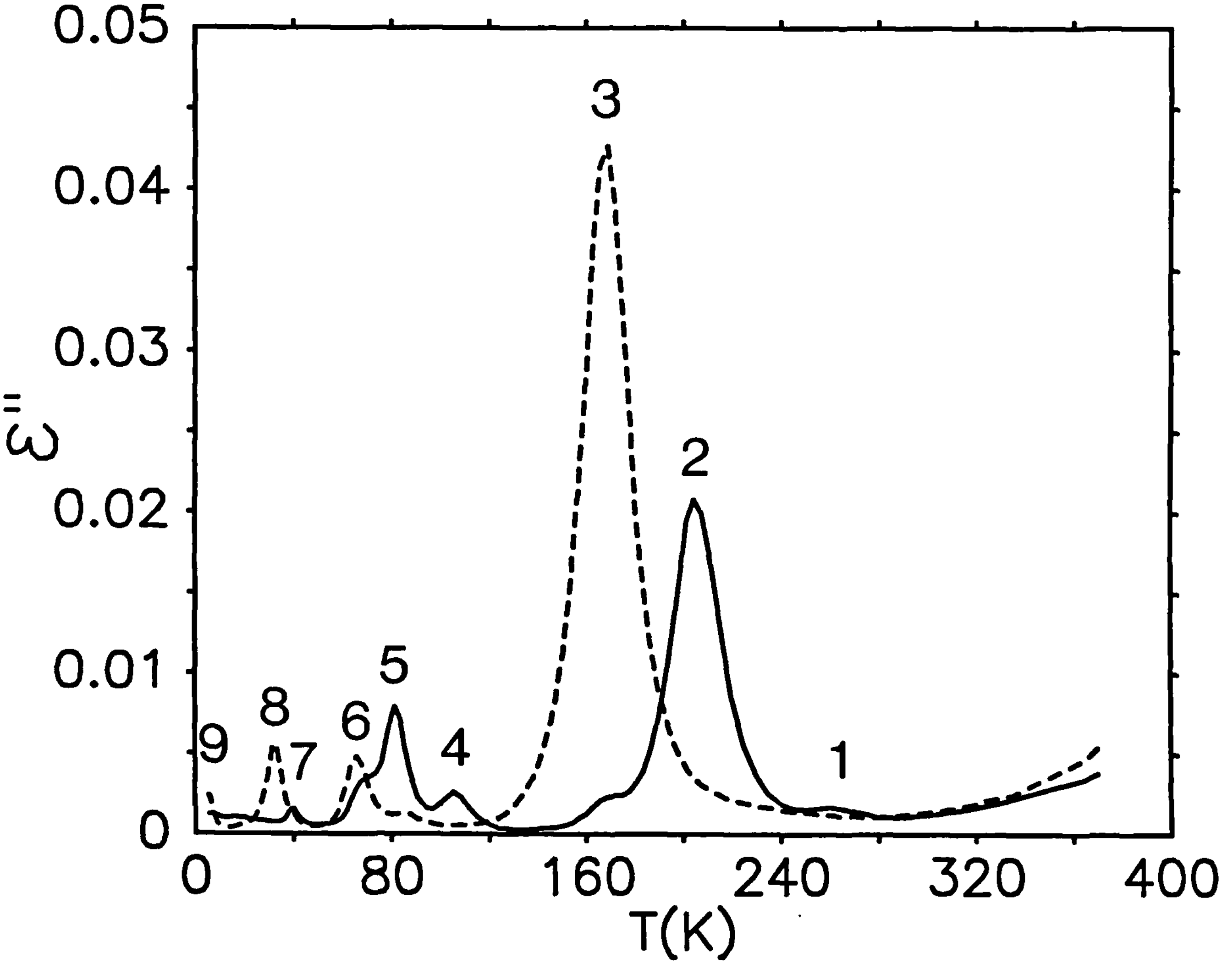
T(K)



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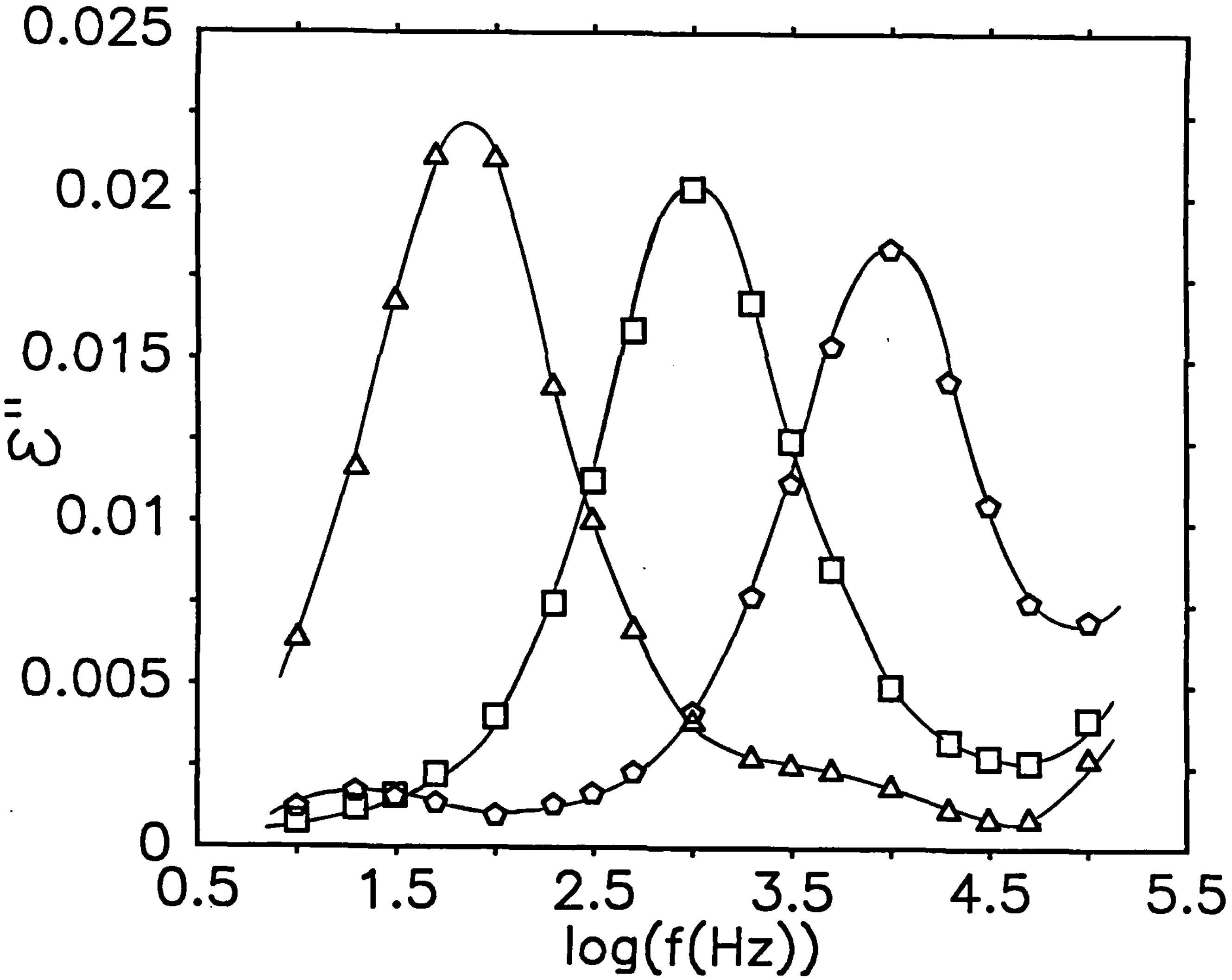
0.025
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ε''
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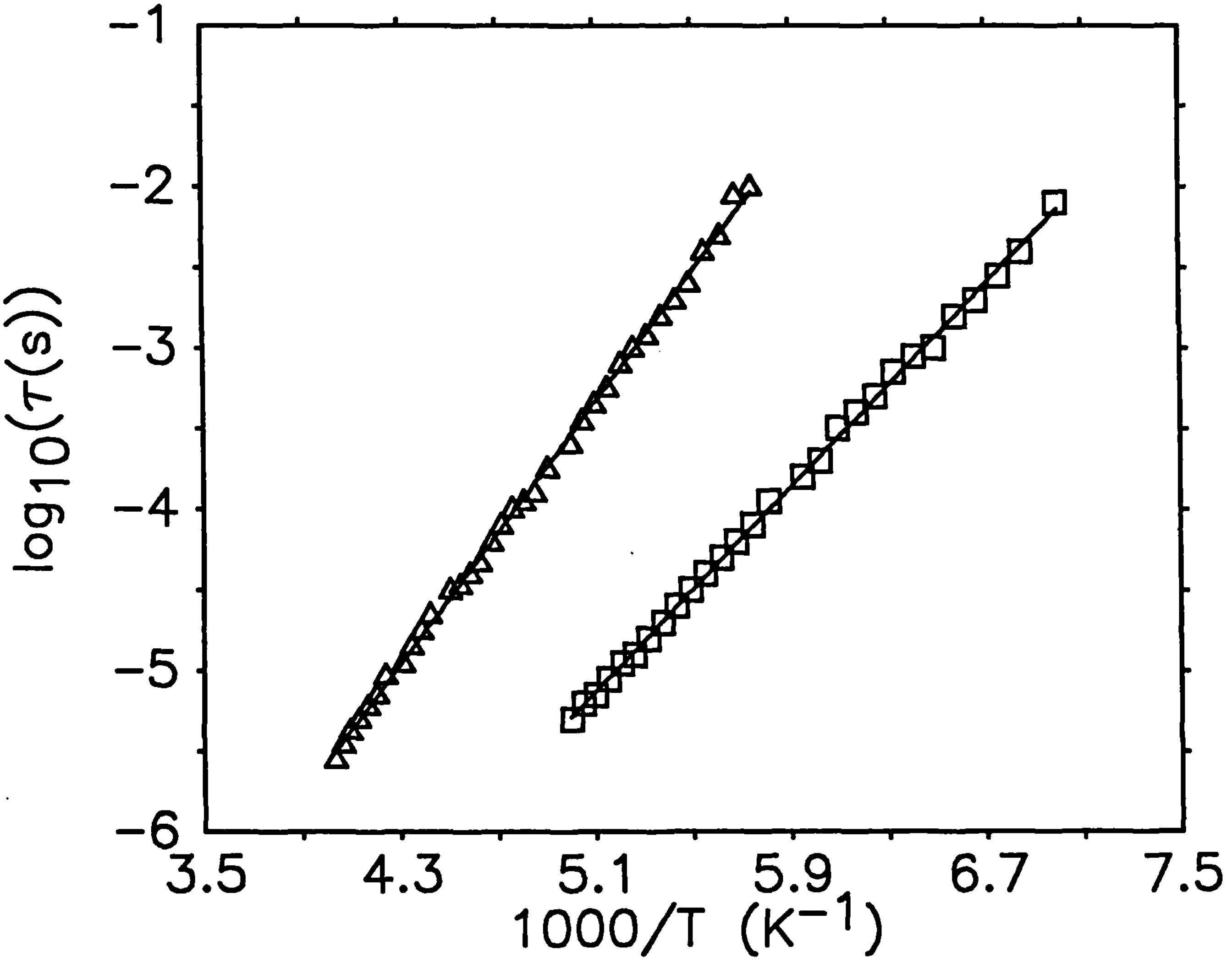
log(f(Hz))



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