Dielectric Properties of Relaxor CuCrO$_2$ at Room Temperature

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The dielectric properties of CuCrO$_2$ bulk and thin films are studied by evaluating the complex dielectric function ε. In addition to the small peak near the Néel temperature T_N, a secondary broad peak is found at high temperatures around $T_m = 450$ K $\gg T_N$. As a feature of relaxor ferroelectrics, the maximum temperature T_m increases with increasing frequency. The real part of ε decreases with increasing magnetic field h and the peak at T_N vanishes. The secondary peak becomes smaller and is broadened with increasing magnetic field. ε increases with increasing film thickness. Near T_m, the dielectric function offers a critical behavior expressed by an exponent $\gamma = 1.74$. Using scaling arguments, critical exponents $\beta = 0.13$ and $\delta = 13.38$ are deduced. The exponents depend on the film thickness. While β increases, the exponent γ is reduced with increasing film thickness.

1. Introduction

Delafossite oxides belong to a family of substances with the general formula ABO$_2$, where A is a monovalent cation as Pt, Pd, Ag, or Cu, whereas B is a trivalent transition metal. Such compounds reveal a rhombohedral crystal structure and show a broad variety of interesting properties.[1–4] In particular,

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CuCrO$_2$ (CCO) exhibits multiferroicity at magnetic ordering temperature (Néel temperature) of $T_N \simeq 24$ K, as shown by Seki et al.[1] Around this temperature, one observes an antiferromagnetic interaction between Cr^{3+} ions, which are aligned in a triangular lattice in the (a, b) plane. Moreover, CCO offers a spin-induced ferroelectricity. The polarization appears below the magnetic phase transition temperature T_N in the absence of magnetic field.[1] The related dielectric properties are studied mainly at low temperatures where the dielectric constant ε shows a kink at T_N.[1,3,5–7] The frequency-dependent dielectric function of CCO nanoparticles at room temperature has been reported by Ahmad et al.[8] Recently, investigations have suggested that at room temperatures CCO behaves like a relaxor-type ferroelectrics[9] with a broad maximum in the dielectric permittivity and its frequency dispersion.

However at low temperatures, the polarization is mainly spin induced[5] and other processes such as relaxation processes[10] could be relevant at higher temperatures. So relaxor ferroelectricity had been studied within an extended random site Ising model with Glauber dynamics.[11] Our approach is focused on the dielectric properties especially at room temperatures, which are manifested by the dielectric function ε. Because at higher temperatures more phonons are excited, our aim is to discuss the relaxor behavior under inclusion of phonon–phonon interaction. Therefore, the aim of our article is the analysis of the dielectric properties of CCO at room temperatures. To that purpose, we evaluate the complex dielectric function ε for CCO bulk material and thin films for the first time. The present calculation is a substantial extension of a previous article[5] where we have studied only the real part of ε at low temperatures, giving rise to a peak at T_N. The high-temperature behavior is characterized by a secondary broad peak, which shows a kind of critical behavior expressed by some exponents γ, β, and δ of the relaxor CCO.

The model is broadly discussed in our previous article[5] at low temperatures. Here the complex magnetic subsystem is characterized by the Heisenberg model. The spin-induced polarization is due to a quadratic magnetoelectric coupling attended by strong anharmonic spin-phonon interactions. As demonstrated in ref. [5] the phonon–phonon interaction is not relevant at low temperatures. As already emphasized, the extension to higher temperatures such as room temperature necessitates the consideration of the previously neglected phonon–phonon interactions. As a new aspect the analytical

calculations reveal a relaxor ferroelectric behavior at higher temperatures, which seems to have originated essentially by the phonon interaction.

2. Model

As already discussed, the present approach intends a substantial extension of our previous paper[5] to higher temperatures, which requires an upgrading of the underlying model. The magnetic properties are still described by the Heisenberg model. Within the triangular (a, b) plane, the Cr^{3+} ions show an antiferromagnetic interaction, whereas between the planes, there appears a ferromagnetic coupling. The quadratic magnetoelectric coupling and strong spin–phonon interactions give rise to a spin-induced nonzero polarization. Because at higher temperatures numerous phonons are well excited, our previous model in ref. [5] is extended by including anharmonic phonon–phonon interactions. The related Hamiltonian reads

$$H_{\text{ph}} = \frac{1}{2!}\sum_i \omega_{0i} a_i a_i^+ + \frac{1}{3!}\sum_{i,j,r} B(i,j,r) Q_i Q_j Q_r$$
$$+ \frac{1}{4!}\sum_{i,j,r,s} A(i,j,r,s) Q_i Q_j Q_r Q_s \quad (1)$$

Q_i and ω_{0i} are the normal coordinate and frequency, respectively, of the lattice mode. Q_i can be expressed in terms of phonon creation a^+ and phonon annihilation a operators.

The main analytical results originate by solving the equation for the dielectric function $\varepsilon(\mathbf{k}, \omega)$:

$$\left((\Lambda/(\varepsilon(\mathbf{k}, \omega) - 1))_{\alpha\beta} + \Lambda \frac{k_\alpha k_\beta}{k^2} \right) G^{\beta\gamma}(\mathbf{k}, \omega) = \delta_{\alpha\gamma} \quad (2)$$

where $\Lambda = 4\pi Z^2/v$, Z is the electron charge and v is the volume. The index $\alpha = 1, 2, 3$ stands for the components. The real and the imaginary part of the dielectric function $\varepsilon'(\mathbf{k}, \omega)$ and $\varepsilon''(\mathbf{k}, \omega)$, respectively, are directly related to the complex valued function, Green's function, G^{zz} (cf. ref. [5]). This longitudinal anticommutator Green's function describes the ferroelectric properties based on the Ising model in a transverse field in terms of pseudospin operators B^z. It is defined by $G^{zz}(\mathbf{k}) = \langle\langle B_k^z; B_{-k}^z \rangle\rangle$. Including correlations beyond simple random phase approximation, we get

$$G^{zz}(\mathbf{k}, E) = \frac{2\langle B^z(\mathbf{k}) B^z(-\mathbf{k})\rangle (E^2 - (E_f(\mathbf{k}))^2 + 2iE\gamma^{11})}{(E^2 - (E_f(\mathbf{k}))^2 + 2iE\gamma^{11})(E + i\gamma^{33}) - E(\varepsilon^{13})^2} \quad (3)$$

Here, $E_f(\mathbf{k})$ and γ^{11} are the transverse pseudospin-wave energy and its damping, whereas γ^{33} is the longitudinal damping. ε^{13} describes the coupling between the longitudinal and transverse modes. Through the magnetoelectric coupling g, the pseudospin exchange interaction constant, J', which determines the pseudospin energy $E_f(\mathbf{k})$ and damping γ^{11} as well as γ^{33}, is renormalized to $J'_{\text{eff}} = J'_0 + 2g(\langle S^- S^+ \rangle + \langle S^z S^z \rangle)$. The correlation functions include the spin–phonon and phonon–phonon interactions and so indirectly influence the dielectric constant, their position, and width.

3. Numerical Results and Discussion

The numerical evaluation is based on analytical results obtained using Green's function technique. In particular, all the model parameters comprised in the Hamiltonian of our model are also included in the expression for the dielectric function. Let us emphasize that the elementary excitations are essential for the calculation of the dielectric function.[5] For completeness, we offer all model parameters used in the present version, too: $J_1 = -2.4$ meV stands for the antiferromagnetic interlayer exchange coupling, $J_2 = 0.012$ meV is the intralayer ferromagnetic exchange interaction strength, $D = 0.033$ meV is a strongly relevant single-site anisotropy,[12] and $S = 3/2$. Although the value of J_2 is much smaller compared with the absolute value of the antiferromagnetic coupling J_1, the interlayer coupling is important for $CuCrO_2$ and hence such a coupling should be taken into account. The spin–phonon interaction is characterized by the couplings $F = 23$ cm^{-1} and $R = -18$ cm^{-1}, which are mainly relevant for low temperatures (cf. ref. [13]). In the high-temperature regime, above $T_N = 24$ K with $M = 0$, the anharmonic phonon–phonon couplings A and B become the decisive parameters, the values of which are given by $B = -3$ cm^{-1} and $A = 6.8$ cm^{-1}. They are deduced from the experimental data of the phonon modes in $CuCrO_2$ as shown by Aktas et al.[14] Notice that the couplings A and B had been neglected at low temperature.[5]

Moreover, let us emphasize that one has to distinguish in relaxor multiferroic CCO between the polarization process at low and at high temperatures. At low temperatures, the polarization is spin induced, which can be expressed by the relation $P_{12} \propto [(\mathbf{S}_1 \cdot \mathbf{r}_{12})S_1 - (\mathbf{S}_2 \cdot \mathbf{r}_{12})S_2]$. Here, $\mathbf{r}_{12}$ is the vector joining neighboring ions at i and j. The spontaneous polarization P_s at high temperatures appears due to relaxation processes, which can be obtained by a method recently proposed by Zhang and Huang.[11]

Based on our analytical results for the dielectric function in Equation (2), we have calculated the real and imaginary part of the dielectric function ε of CCO for $0 \leq T \leq 550$ K. The temperature dependence of the real part ε' is shown in **Figure 1**.
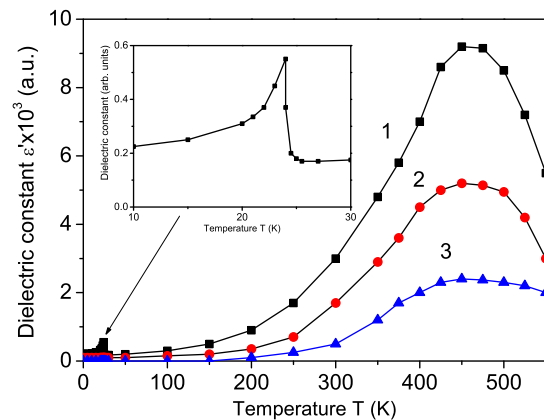

Figure 1. Temperature dependence of the real part of the dielectric constant ε' of bulk CCO for different magnetic fields h: $h = 0$ (1); $h = 50$ kOe (2); and $h = 70$ kOe (3).

One observes that ε' is very small at low temperatures, which could be related to a freezing of dipoles. At the Néel temperature $T_N = 25$ K the small peak due to strong spin–phonon interactions, already theoretically proposed in ref. [5], is reproduced, as shown in the inset in Figure 1. Notice that such a small peak is also observed experimentally in other papers.[1,3,6,7] Mostly, the experimental data of CCO are obtained in the low-temperature regime. With increasing temperature, ε' increases likewise. Related to the growth of the real part, there occurs a peak in the imaginary part ε'' around 350 K, compare **Figure 2**. The peak in ε'' indicates a thermal relaxation in this temperature range. Generally, it can be supposed that CCO exhibits multiferroicity at low temperatures and interesting dielectric properties at higher temperatures, well above the magnetic transition temperature. Our analysis reveals an additional broad peak in ε' in the high-temperature regime near $T_m \simeq 450$ K. Such a secondary peak was recently observed by experimental investigations of CCO in the study by Pokhriyal et al.[9] Based on a careful analysis of XRD data in the study,[9] the authors have associated the appearance of that extra peak with distorted CrO_6 octahedra, giving rise to strained regions which are polar in the otherwise nonpolar matrix. As argued by Pokhriyal et al.,[9] such polar regions could lead to the observed relaxor-type ferroelectricity.

Another investigation in the study by Ahmad et al.[8] showed that dielectric constant ε' offers a maximum at temperature $T_m = 373$ K for CCO nanoparticles. The measured broad peak in ε' of CCO is a feature of relaxor ferroelectrics.[7,15,16] Closely related to this broad peak in the real part of the dielectric function ε' is the appearance of a broad minimum in the imaginary part of the dielectric function ε'' around the maximum temperature $T_m \simeq 450$ K. Such a behavior is shown in Figure 2. The earlier observed minimum broad peak in ε'' around 350 K could be identified with contribution from a relaxation polarization process, which originates from thermally activated flip processes of polar regions. Moreover, a small anomaly occurs, a slight increase in ε'' is additionally observed at T_N; see inset in Figure 2. Notice that Pokhriyal et al.[9] investigated ε in a temperature interval of $100 \leq T \leq 480$ K. The authors[9] reported near $T \approx 200$ K a step-like increase in ε' additionally to the broad peak around $T_m \simeq 445$ K, whereas ε'' exhibits two maxima around
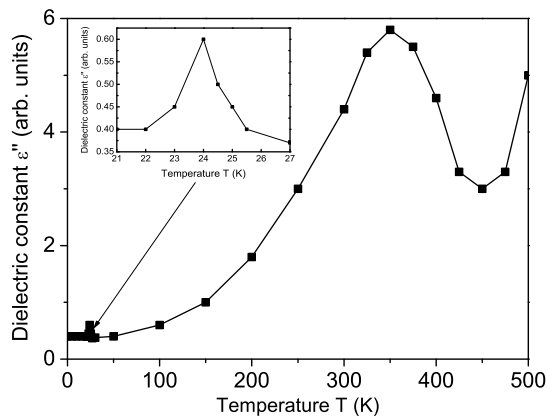
200 and 350 K. Our study does not give rise to a step-like increase in ε' near $T \simeq 200$ K, as supposed by Pokhriyal.[9] Otherwise, the authors of that study[9] do not see the peak at T_N.

Applying an external field h, the dielectric constant ε' decreases, which can be considered as an indirect evidence for the multiferroic behavior of CCO. The first small peak at T_N vanishes, whereas the second one at $T \simeq 450$ K is smaller and broader, which is shown in Figure 1, curves 2 and 3. The observed result for $\varepsilon'(h)$ in the low-temperature region is in agreement with the experimental findings in the study by Poienar et al.[3] Measurements of the magnetic field dependence of ε' at room temperature are still missing.

A feature of relaxor ferroelectrics is the frequency dependence of the temperature at the broad maximum T_m. The frequency dependence of the dielectric function follows independent polarization processes from Kramers–Kronig's equations.[17] Relaxors are characterized by frequency-dependent diffuse phase transitions. The maximum in ε' is diffusive, accompanied by a strong dispersion of dielectric maximum temperature $T_m \simeq 450$ K with frequency (see Figure 1). The dielectric maximum is shifted toward higher temperatures with an increase in the frequency, which signifies the relaxor behavior of CCO.[9] This dependence could be described by the empirical Vogel–Fulcher relation for the dielectric relaxation in relaxor ferroelectrics,[18] according to which the polarization flipping frequency f related to the activation energy E_a is as follows.

$$f = f_0 \exp\left[\frac{E_a}{k(T_m - T_f)}\right] \tag{4}$$

where T_f is the freezing temperature.

In **Figure 3**, it is shown that T_m increases with increasing frequency, in agreement with several experimental data.[9,19–21] Let us stress that such a frequency dependence is not observed in conventional ferroelectrics such as $BaTiO_3$.

As already mentioned, the peak observed in the dielectric constant at $T_m \simeq 450$ K is not so pronounced, as expected in conventional ferroelectrics.

To confirm the relaxor behavior in CCO, we calculate the critical exponent γ of the temperature dependence of ε'. In general, relaxor ferroelectrics offers a strong deviation from Curie–Weiss'

Figure 2. Temperature dependence of the imaginary part of the dielectric constant ε'' of bulk CCO for zero magnetic field.
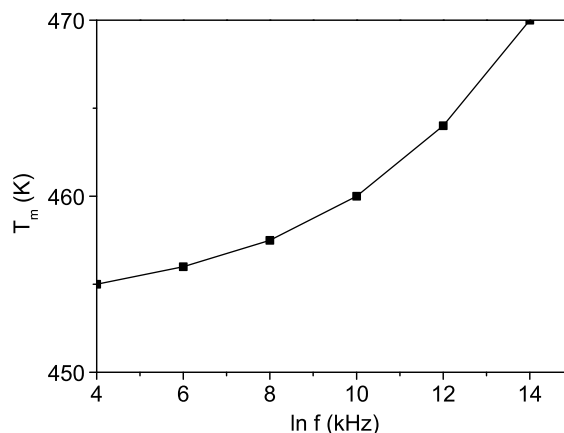

Figure 3. Frequency dependence of the maximum temperature T_m of ε'.

law, as suggested by Uchino et al.[22] The modification is due to the diffuseness of the phase transition. It reads as

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = C'^{-1}(T - T_m)^\gamma \qquad (5)$$

where ε_m is the maximum of the dielectric constant and T_m the related temperature, C' is a constant, and γ yields information concerning the character of the phase transition; the exponent characterizes the slope of the curve.

In case $\gamma = 1$, the usual Curie–Weiss law is indicated, whereas a value $\gamma = 2$ stands for a complete diffusive phase transition. As an example let us notice that in pure BaTiO$_3$ an exponent $\gamma = 1.08$ is observed, where the deviation from the value $\gamma \simeq 1$ is due to fluctuations. The value for the exponent γ grows to $\gamma \simeq 2$ in case of a diffusive phase transition occurring in doped BaTiO$_3$.[15,23–25] As dopants, one applies La, Ce, or Zr. Our best fit of the curve $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$ gives an exponent $\gamma \simeq 1.74$, as shown in **Figure 4**. The value for γ is strong evidence for the relaxor-type behavior of CCO. It is also in quite good agreement with that one presented in the study by Pokhriyal et al.,[9] where $\gamma = 1.76$ at 10 kHz. Using the scaling law $\alpha + 2\beta + \gamma = 2$, we can estimate the exponent β for the order parameter, for instance, the polarization $P = P_0(1 - T/T_C)^\beta$. The exponent α is related to the heat capacity, $C \propto (1 - T/T_C)^{-\alpha}$. Values for α are still missing especially for CCO. Otherwise, the exponent is rather small, as in some other magnetic, relaxor ferroelectric materials; see other studies.[26,27] Therefore, we have chosen $\alpha \approx 0$. Based on the scaling law, we find $\beta \approx 0.13$ as the exponent for the order parameter P.

A comparable value for the exponent $\beta \approx 0.13 - 0.15$ is reported for other relaxor ferroelectrics.[26–29] Using another scaling law $\beta + \gamma = \delta\beta$, we can estimate the exponent δ. That exponent describes the change of the polarization with an applied electric field at the critical isotherm according to $P(E) \approx E^\delta$. The value $\delta \simeq 13.38$ is high but comparable with the value of the 2D Ising model.

The dielectric constant ε' is also analyzed for a CCO thin film with different number N of layers. Taking into account that the exchange interaction on the surface layers J_s can be different from the one in the bulk material J_b, we find a significant
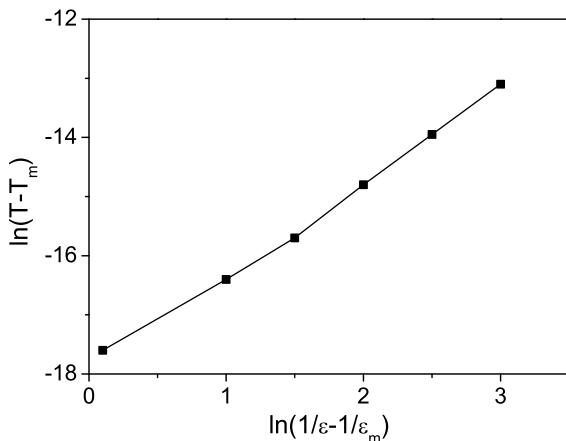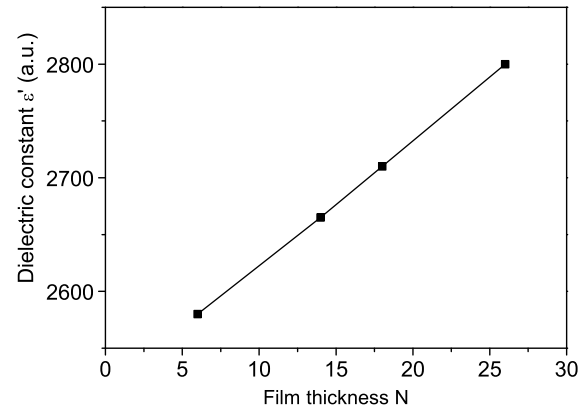
Figure 5. Film thickness dependence of the dielectric constant ε' at $T = 300$ K in CCO.
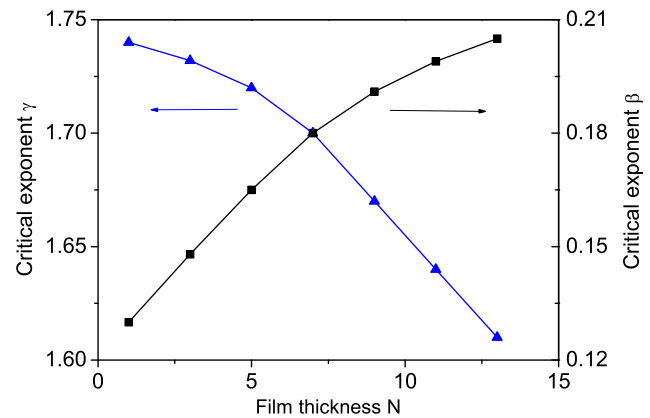
Figure 6. Film thickness dependence of the critical exponents γ and β in CCO.

lowering of the dielectric constant in CCO thin films compared with bulk CCO material. In our case, we used $J_s < J_b$. The result for ε shown in **Figure 5** is in agreement the experimental data presented in other studies.[30,31] Figure 5 shows a nearly linear film thickness dependence of ε'.

The related critical exponent γ decreases, whereas β increases with increasing film thickness N, which is shown in **Figure 6**. This behavior is confirmed by many experimental and theoretical works for different nanostructures; see various studies.[32–34]

4. Conclusion

To conclude, we have studied the real and the imaginary part of the dielectric function ε in CCO in both bulk and thin films at high temperatures using a microscopic model including magnetic interaction via Heisenberg coupling, anharmonic spin–phonon interaction, and phonon–phonon coupling. Moreover, a magnetoelectric coupling is considered. The numerical evaluation based on analytical calculations gives rise to a small peak at $T_N = 25$ K, as already discussed before. As a new result, we observe a broad peak in ε' around $T_m \approx 450$ K. The real part

Figure 4. Plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T - T_m)$.

of the dielectric function ε' decreases, whereas the maximum temperature T_m increases with increasing frequency. The dielectric constant ε' decreases, the peak at T_N vanishes, whereas the second one is smaller and becomes broader with increasing magnetic field h. The critical exponent γ for the dielectric constant ε is found to be $\gamma = 1.74$. Other exponents are estimated using scaling laws. So we get $\beta = 0.13$ and $\delta = 13.38$. For CCO thin films, ε and β increase, whereas γ decreases with increasing film thickness. The results are in reasonable agreement with experimental data.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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