Femtosecond tunneling of polarons in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$

A. Levstik*, C. Filipič, G. Tavčar and B. Žemva
Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
*adrijan.levstik@ijs.si

Received 21 February 2014; Accepted 15 June 2014; Published 28 July 2014

The complex dielectric constant/ac electrical conductivity was investigated as a function of frequency and temperature in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The system undergoes a ferroelectric phase transition at higher temperatures. At lower temperatures the real part of the complex ac electric conductivity was found to follow the universal dielectric response (UDR) $\sigma' \propto \nu^s$, typical for hopping or tunneling of localized charge carriers. A detailed analysis of the temperature dependence of the UDR parameter s in terms of the theoretical model for tunneling of small polarons revealed that, at low temperatures, this mechanism governs the charge transport in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The value of the inverse attempt frequency τ_0 indicates the femtosecond tunneling of polarons in the system similar to the Büttiker–Landauer transversal time.

Keywords: Low-field transport; tunneling; polarons and electron–phonon interactions.

1. Introduction

In attosecond physics, experimental investigations of atomic interactions with intense laser fields have demonstrated tunneling times of electrons in different time scales from 10^{-12} to 10^{-18} s, depending on electron motion on atomic or molecular scales.¹

In the present paper, we show that similar tunneling times of polaronic electrons are observed from the classical experiment where tunneling time is determined via measurements of frequency and temperature dependence of dielectric constant and electrical conductivity and their analysis using the theoretical model describing small polarons. We show that polarons play an important role in magnetoelectric² $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ as the dominant charge transport mechanism at low temperatures.

Magnetoelectric systems are at the cutting edge of present day material science, since the possibilities of electric field control of magnetism and vice versa allow, among other things, an electric readout of magnetically stored information, magnetic capacitors, new spintronic elements and various sensors.³

2. Experiment

Polycrystalline $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ was prepared by reacting CrF_3 with PbF_2 in a 3:5 molar ratio. The reaction mixture was placed in a gold reaction vessel, sealed, and heated for 48 h at 800 K, as described previously.⁴

The complex dielectric constant $\varepsilon^*(\nu, T) = \varepsilon' - i\varepsilon''$ was measured between 50 and 650 K in the frequency range of 1 Hz to 1 MHz, using a Novocontrol Alpha High Resolution Dielectric Analyzer. The amplitude of the probing ac electric

signal was 1 V/mm. The temperature was stabilized within ± 0.1 K using an Oxford Instruments continuous flow cryostat. The real part of the complex ac conductivity $\sigma^*(\nu, T) = \sigma' + i\sigma''$ was obtained from $\sigma' = 2\pi\nu\varepsilon_0\varepsilon''$, with ε_0 being the permittivity of the vacuum.

3. Results and Discussion

$\text{Pb}_5\text{Cr}_3\text{F}_{19}$ is ferroelectric below $T_C = 540$ K. The temperature dependence of the dielectric constant was measured at three frequencies (Fig. 1) and the dielectric constant reveals the ferroelectric phase transition at 540 K. High-temperature EPR spectra supported the occurrence of the para-ferroelectric transition. A phase transition at 545 K, where the temperature dependence of EPR susceptibility, the line width δH , and the g -factor show pronounced step in their values, was demonstrated by Blinc *et al.*^{2,5} An antiferro-magnetic transition was also observed with $T_N \sim 11$ K.² Results of low-temperature EPR spectra were confirmed by magnetic measurements. No magnetic hysteresis loops exist below 11 K, thus excluding ferromagnetic, ferrimagnetic, and spin glass order, but the relationship between magnetization and magnetic field is not linear. The observed changes of the magnetic properties ongoing through the ferroelectric phase transition exhibit magnetoelectric coupling.²

In order to characterize $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ at low temperatures, the temperature dependence of the complex dielectric constant/ac electrical conductivity, as a function of the frequency, was investigated in detail. The temperature dependence of the real part of the complex ac conductivity, σ' , in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, was measured at several frequencies (Fig. 2). Below 300 K, σ' is seen to be almost independent of temperature till 10 K while,

Fig. 1. Temperature dependence of the dielectric constant in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, measured at three frequencies.

Fig. 2. Temperature dependence of the real part of the complex ac electrical conductivity, σ' , in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, measured at several frequencies.

at higher temperatures, it becomes strongly temperature dependent. Moreover, at higher temperatures still, with reduced measuring frequency, σ' tends towards linear dependence, suggesting that the dc conductivity might reveal thermally activated behavior. The strongly frequency-dependent plateaus in $\sigma'(T)$ below 300 K suggest that hopping or tunneling of localized charge carriers governs the electrical transport at lower temperatures.⁶

The temperature dependence of the ac electrical conductivity, σ' , measured at 1 Hz, (Fig. 3) is close to that of the dc conductivity. $\ln(\sigma')$ tends towards a linear dependence on $1/T$, therefore the activation energy, E_{dc} , was determined from the slope using the equation for hopping of small polarons.^{7,8}

Polarons are best identified in measurements with charge carriers in nonmetals or doped semiconductors.⁹ The concept of polarons can represent the basis for understanding the complex physical properties of strongly correlated electronic systems exhibiting high-temperature superconductivity or the colossal magnetoresistance.¹⁰ In fact, besides the occurrence of mid-infrared excitation in the optical conductivity,^{11,12} the fingerprint of polarons is usually associated with the temperature and frequency dependence of the ac conductivity.

Fig. 3. $\ln(\sigma')$, measured at 1 Hz, as a function of the inverse temperature.

Fig. 4. (a) Frequency dependence of the real part of the complex electrical conductivity, σ' , in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ at five selected temperatures. The solid lines are fits, performed simultaneously, for $\sigma'(\nu)$ and $\varepsilon'(\nu)$ to an expression combining a dc contribution, a UDR hopping contribution, a ν^n power law, and a limiting high frequency dielectric constant ε_∞ . The straight line indicates the slope with $n = 1$. (b) Frequency dependence of the real part of the complex dielectric constant, ε' , at the same temperatures as above. The solid lines are fits, performed simultaneously for $\sigma'(\nu)$ and $\varepsilon'(\nu)$, with the same contributions as in (a).

The frequency dependence of the ac electrical conductivity in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ was measured at five selected temperatures (Fig. 4(a)). At lower frequencies, $\sigma'(\nu)$ starts to saturate towards the dc conductivity. At higher frequencies, σ' follows

a power law $\sigma' = \sigma_2 \nu^n$ with $n \approx 1$ and, at the lowest temperatures, this behavior was observed over a broad frequency range of four decades. It is however known¹³ that the simple ansatz $\sigma'(\nu) = \sigma_{dc} + \sigma_2 \nu^n$ cannot describe $\sigma'(\nu)$ properly over the broad frequency range studied here. Figure 4(b) shows the frequency dependence of the real part of the dielectric constant at five selected temperatures as before. At higher frequencies, $\varepsilon'(\nu)$ starts to saturate towards the high-frequency dielectric constant ε_∞ .

For many amorphous and crystal systems it has been shown that, besides the dc contribution of conductivity, σ_{dc} , the frequency-dependent real part of complex ac conductivity, σ' , follows the so-called universal dielectric response (UDR). An additional sub-linear term, $\sigma' = \sigma_1 \nu^s$ with $s \leq 1$, was therefore introduced. The UDR contribution has been predicted by various models^{14,15} and is the most common approach to take into account the hopping conductivity of localized charge carriers.

Under these assumptions, complex conductivity $\sigma^*(\nu) = \sigma'(\nu) + i\sigma''(\nu)$ is given by^{16,17}

$$\begin{aligned}\sigma'(\nu) &= \sigma_{dc} + \sigma_1 \nu^s, \\ \sigma''(\nu) &= \tan(s\pi/2) \sigma_1 \nu^s = \nu \varepsilon_0 \varepsilon'(\nu).\end{aligned}$$

Here, σ_1 is a temperature-dependent constant, ν is the measuring frequency, s the frequency exponent, $s \leq 1$, and ε_∞ being permittivity of the vacuum. From conductivity, the complex dielectric permittivity can be calculated by $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) = i\sigma^*(\nu)/\nu\varepsilon_0$.

The expression for the frequency dependence of the dielectric constant, $\varepsilon'(\nu) = \varepsilon_\infty + \varepsilon_1 \nu^{s-1} + \varepsilon_2 \nu^{n-1}$, is obtained by the Kramers–Kronig transformation, therefore for $n = 1$

$$\varepsilon_1/\sigma_1 = \tan(\pi s/2)/\varepsilon_0.$$

The above equation connects parameters ε_1 and σ_1 , and limits the simultaneous fits of $\sigma'(\nu)$ and $\varepsilon'(\nu)$.

From equations, for $\sigma'(\nu) = \sigma_{dc} + \sigma_1 \nu^s + \sigma_2 \nu^n$ and $\varepsilon'(\nu) = \varepsilon_\infty + \varepsilon_1 \nu^{s-1} + \varepsilon_2 \nu^{n-1}$, we derive (for $n = 1$)

$$\begin{aligned}\sigma'(\nu) &= \sigma_{dc} + \sigma_1 \nu^s + \sigma_2 \nu, \\ \varepsilon'(\nu) &= \varepsilon_\infty + [\sigma_1 \tan(s\pi/2)/\varepsilon_0] \nu^{s-1},\end{aligned}$$

which we use for simultaneous fitting of $\sigma'(\nu)$ and $\varepsilon'(\nu)$ data. The solid lines in Figs. 4(a) and 4(b) were obtained by simultaneous fits of the experimental $\sigma'(\nu)$ and $\varepsilon'(\nu)$ data to the above expressions. To justify the choice $n = 1$ we added the limiting line, $\sigma' \propto \nu^n$ with $n = 1$, to Fig. 4(a).

Figure 5 shows the temperature dependence of the exponent s for $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The UDR exponent s , which was determined by the above mentioned fitting procedure, shows non-monotonous temperature dependence with a minimum at approximately 360 K. Such behavior is predicted by the tunneling polaron model^{14,15,18} (originally this model was developed for tunneling of overlapping large polarons,^{14,15} but it was argued later¹⁸ that it is in fact applicable to small polarons), which gives the temperature dependence of s as^{14,15}

$$s = 1 - \frac{4 + 6W_\infty r'_0/(kTR^2)}{R'[1 + W_\infty r'_0/(kTR^2)]^2}, \quad (1)$$

Fig. 5. Temperature dependence of the UDR parameter s , for $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, determined from the simultaneous fits of the experimental $\sigma'(\nu)$ and $\varepsilon'(\nu)$ data (as presented in Fig. 4). The solid line is the fit to a model for small polaron tunneling [Eqs. (1) and (2)].

where W_∞ denotes the energy barrier and r'_0 the reduced polaron radius. The reduced tunneling distance R' is also a function of W_∞ and r'_0 and, additionally, of the inverse attempt frequency τ_0 as^{14,15}

$$\begin{aligned}2R' &= \ln \frac{1}{\omega \tau_0} - \frac{W_\infty}{kT} \\ &+ \left[\left(\ln \frac{1}{\omega \tau_0} - \frac{W_\infty}{kT} \right)^2 + \frac{4r'_0 W_\infty}{kT} \right]^{1/2}, \quad (2)\end{aligned}$$

where $\omega = 2\pi\nu$. We are aware that the model predicts a frequency dependence of s and therefore equation $\sigma'(\nu) = \sigma_{dc} + \sigma_1 \nu^s$ should no longer be valid in a strong sense, i.e., with $s = \text{constant}$. However, in the present data a pure ν^s contribution is seen only over a relatively small frequency range and it can be assumed that the rather weak $\ln(\nu)$ dependence of R' leads to only small deviations from Eq. (1). Fitting the $s(T)$ data to Eqs. (1) and (2) (denoted by the solid line in Fig. 5) yields values of $W_\infty = 0.89$ eV, $r'_0 = 0.69$, and $\tau_0 = 2 \times 10^{-15}$ s.

From the detected $\sigma'(\nu, T)$, $\varepsilon'(\nu, T)$, and $s(T)$ values we can conclude that tunneling of polarons is the dominating charge transport mechanism in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ at temperatures below 420 K.

In the model, in which tunneling of polarons is the dominant mechanism, an overlap of regions of lattice distortion is important.¹⁴ The height of the effective barrier, W , depend on the tunneling distance (R) and radius of the polaron (r_0): $W = W_\infty(1 - r_0/R)$, where the polaron energy is $W_\infty = e^2/(4\pi\varepsilon_0 r_0 \varepsilon_p)$ and $\varepsilon_p^{-1} = \varepsilon_\infty^{-1} - \varepsilon_s^{-1}$, where ε_∞ is the high frequency and ε_s static dielectric constant.

The dielectric relaxation connected with polarons can be analyzed with the electrical modulus picture¹⁹ in order to determine the high frequency and static dielectric constants. An electric modulus M^* is defined as the reciprocal of dielectric constant¹⁹ ε^*

$$M^* = 1/\varepsilon^* = M'(\nu) + iM''(\nu),$$

Fig. 6. (Color online) M'' versus M' at four temperatures in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$. The solid lines serve as a guide for the eye. M_∞ is extrapolated by the red straight line at high frequencies.

where

$$M'(\nu) = \frac{\varepsilon'(\nu)}{(\varepsilon'(\nu))^2 + (\varepsilon''(\nu))^2}$$

and

$$M''(\nu) = \frac{\varepsilon''(\nu)}{(\varepsilon'(\nu))^2 + (\varepsilon''(\nu))^2}$$

are the real and imaginary part of complex modulus, respectively.

M'' versus M' at four temperatures in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ is presented in Fig. 6. From the Cole–Cole diagram it is possible to determine $M'_\infty = 0.031$ at high frequencies, and M'_s , which approaches close to zero, at low frequencies.

From the values for $M'_\infty = 1/\varepsilon_\infty$ and $M'_s = 1/\varepsilon_s$ we can determine the value of the polaron radius r_0 from the expressions $W_\infty = e^2/(4\pi\varepsilon_0 r_0 \varepsilon_p)$ and $\varepsilon_p^{-1} = \varepsilon_\infty^{-1} - \varepsilon_s^{-1}$. The coefficient α can also be determined using the relation¹⁴ that connects the reduced polaron radius and the polaron radius ($r'_0 = 2\alpha r_0$). The values of fitting parameters for $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, Mn_1 ($38.9\text{LiI}-1.0\text{AgI}-60\text{B}_2\text{O}_3: 0.1\text{MnO}$),²⁰ and for A_6 ($6\text{B}_2\text{O}_3-34\text{Fe}_2\text{O}_3-60\text{P}_2\text{O}_5$),²¹ previously determined, are given in Table 1. In the last column, the oscillation period of an electron¹ $T_{\text{osc}} = 2\pi(\hbar/\Delta W)$ is given if we take $\Delta W \sim W_\infty$. Reciprocal attempt frequency of a polaron can be compared with the oscillation period of an electron and with the Büttiker–Landauer transversal time which is determined²² for electrons in helium between 0.45×10^{-15} and 0.56×10^{-15} s.

Table 1. Polaron parameters of samples.

Sample	W_∞ (eV)	r'_0	r_0 (Å)	τ_0 (s)	α (Å ⁻¹)	E_{dc} (eV)	T_{osc} (s)
$\text{Pb}_5\text{Cr}_3\text{F}_{19}$	0.89	0.69	0.51	2×10^{-15}	0.68	1.08	1.2×10^{-14}
Mn_1 (Ref. 20)	1.1	0.50	1.06	2×10^{-15}	0.24	0.88	0.96×10^{-14}
A_6 (Ref. 21)	0.92	0.92	0.84	2×10^{-16}	0.55	0.95	1.1×10^{-14}

4. Conclusion

In conclusion, the dielectric constant and ac electrical conductivity in $\text{Pb}_5\text{Cr}_3\text{F}_{19}$ were investigated over broad frequency and temperature ranges. The ferroelectric phase transition was observed at high temperature (540 K). The changes in magnetic properties observed at the ferroelectric phase transition provide evidence for a magnetoelectric coupling. At low temperatures the real part of the complex ac electric conductivity was found to follow the universal dielectric response $\sigma' \propto \nu^s$, being typical for hopping or tunneling of localized charge carriers. A detailed analysis of the temperature dependence of the UDR parameter s in terms of the theoretical model for tunneling of small polarons revealed that, at low temperatures, this mechanism governs the charge transport in this system. We compared the polaronic parameters of three systems $\text{Pb}_5\text{Cr}_3\text{F}_{19}$, Mn_1 , and A_6 . The reciprocal attempt frequency has values from 2×10^{-15} to 2×10^{-16} s. Comparison, of these values with those for the oscillation period for electrons and for the Büttiker–Landauer transversal time for electrons, shows that there is good agreement.

Acknowledgments

Research was supported by the Slovenian Research Agency (P1-0125). We acknowledge V. Bobnar for high temperature dielectric measurements.

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