Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Aspects of Take Temperature Dependence of Electrical Conductivity in Polymeric Materials

P. Love [a]

[a] Chemistry Department, University of Connecticut at Stamford, Scofieldtown Rd., Stamford, Connecticut, 06903

Version of record first published: 20 Apr 2011.

To cite this article: P. Love (1984): Aspects of Take Temperature Dependence of Electrical Conductivity in Polymeric Materials, Molecular Crystals and Liquid Crystals, 106:3-4, 331-343

To link to this article: http://dx.doi.org/10.1080/00268948408071451

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 331-343
0026-8941/84/1064-0331/$18.50/0

Printed in the United States of America

ASPECTS OF THE TEMPERATURE DEPENDENCE OF ELECTRICAL CONDUCTIVITY IN POLYMERIC MATERIALS

P. LOVE
Chemistry Department,
University of Connecticut at Stamford,
Scofieldtown Rd., Stamford, Connecticut 06903

The temperature dependence of the electrical conductivity of a number of polymeric organic and inorganic materials is described by a function, G(E,T), that is the derivative of the Fermi function. The mathematical justification for the use of this function in place of the Fermi function is described. Use of the G(E,T) function in the appropriate conductivity equation allows one to reproduce the temperature dependence of electrical conductivity in materials as diverse as $(SN)_x$ and germanium single crystals. The function is found to be applicable to experimental conductivity data that collectively span a range of about 20 orders of magnitude, and a total temperature range of approximately 1000 K for the materials cited. The G(E,T) function adequately simulates the commensurate-incommensurate transition that is observed in materials such as $(TMTSF)_2PF_6$ and TTF-TCNQ. The importance of lattice order and the degree of single crystal perfection on derived properties of the conductivity curve are discussed. The G(E,T) function is applicable to other electron transport properties. The temperature dependence of electrical capacitance of $SrTiO_3$ is cited as an example.

INTRODUCTION

The temperature dependence of the electrical conductivity, $\sigma(T)$, is a function that is often discussed in the characterization of low-dimensional polymeric materials. Yet this function has not been expressed by a theoretical equation that adequately accounts for the diverse forms of $\sigma(T)$ that are often observed. One would like to know what constitutes "normal" conductivity, for example, for a metal-insulator transition, and what type of conductivity behavior can be considered atypical for a given material.

One form of electrical conductivity as a function of energy, E, and temperature, T, $\sigma(E,T)$, is that given by the equation,

$$\sigma(E,T) = n(E,T)\ \bar{e}\ \mu(E,T) \qquad (1)$$

where $n(E,T)$ is the electron density in the conduction band,

$$n(E,T) = \int_{E(\text{bottom})}^{E(\text{top})} N(E,T)\ f(E,T)\ dE\ . \qquad (2)$$

The electron charge is represented by $\bar{e}$, and $\mu(E,T)$ is the electron mobility. The Fermi function is, as usual, given by $f(E,T)$ where

$$f(E,T) = \left\{1 + \exp[(E - E_F)/kT]\right\}^{-1}\ . \qquad (3)$$

The term $N(E,T)$ is the electron density of states function.

The function $\sigma(T)$ has been discussed in terms of the temperature dependence of the electron mobility(1). However, this concept has limited applicability particularly with respect to materials that exhibit a metal-insulator, commensurate-incommensurate, or Peierls transition. One explanation for the $\sigma(E,T)$ function must be given in the incommensurate metallic region, and another quite often different one for the commensurate insulator region.

An alternative approach to the calculation of

$\sigma(E,T)$ is to assume that $\mu(E,T)$ is constant to a first approximation, and consider that the temperature dependence of the conductivity is a function of the temperature dependence of the electron density in the conduction band. If this is assumed to be true, and $N(E,T)$ is essentially temperature independent, one could postulate that $\sigma(E,T)$ varies due to the temperature dependence of $f(E,T)$. This, however, is equally unsatisfactory. It is well known that the Fermi function predicts that the electron density in the conduction band tends to zero as the absolute temperature approaches zero. Unless one invokes an electron-phonon or similar scattering mechanism, $\sigma(T)$ for a metallic substance should tend to zero as the temperature approaches absolute zero. Furthermore, Peierls' conclusion that a one-dimensional metal is inherently unstable against a distortion of the lattice is generally cited (2) as accounting for observed metal-insulator transitions.

Neither of these predictions is verified for $\sigma(E,T)$ by analytically pure well ordered single crystals of polysulfur nitride, $(SN)_x$ (3). It is well known that high quality single crystals of $(SN)_x$ exhibit a monotonically increasing conductivity with decreasing temperature, and become superconducting at ~ 0.3 K (4). The low temperature properties of $(SN)_x$ are often overlooked in discussing the behavior of the Fermi function and the inherent instability of low-dimensional materials with respect to a metal-insulator transition.

Disordered or low purity $(SN)_x$ crystals undergo a metal-insulator transition with decreasing temperature, and have lower conductivity (5). Although there are many explanations of these and related facts about $\sigma(E,T)$, none has previously effectively reconciled the behavior of this function for analytically pure high quality single crystals and lower quality disordered single crystals without invoking differences in dimensionality (6), or one explanation for monotonically increasing conductivity and superconductivity on the one hand, and another explanation when a metal-insulator transition occurs on the other.

THE PROBABILITY DENSITY FUNCTION AND ELECTRICAL CONDUCTIVITY

In two papers that will be designated as I (7) and II (8), it has been shown that these problems can be resolved by the proper choice of the probability density function for electron occupancy in the conduction band. Most writers on solid state physics and statistical physics (9) assume that $f(E,T)$ is the probability density function. It is shown in II that the correct probability density function for thermal excitation of valence electrons into the conduction band is the derivative of the Fermi function. The temperature dependence of the electron density in the conduction band is then expected to be proportional to the derivative of the Fermi function with respect to temperature, $G(E,T)$. The correct form of $\sigma(E,T)$ is then given by replacing $f(E,T)$ with $G(E,T)$ in equation 2 where

$$G(E,T) \equiv \frac{\partial(f(E,T))}{\partial T} = \frac{E - E_F}{kT^2} \frac{\exp[(E - E_F)/kT]}{[f(E,T)]^{-2}} . \quad (4)$$

The integral in equation 2 represents integration with respect to energy in the conduction band. The terms of $E - E_F$ in $f(E,T)$ and $G(E,T)$ refer to energy in the band gap region, that is below the conduction band. The quantity $E - E_F$ can be considered to a first approximation to be a constant that is independent of temperature for any given sample. Then $G(E,T)$ in the integral of equation 2 can be considered to be a constant with respect to integration.

The temperature dependence of the conductivity for equation 1 should then be given by the temperature dependence of the function $G(E,T)$. The temperature dependence of $G(E,T)$ should describe the observed behavior of $\sigma(T)$ for materials such as $(SN)_x$ in both high quality single crystal form, and for lower quality disordered crystals. The conductivity of a high quality single crystal of $(SN)_x$ (10), and that predicted in terms of curve fitting $G(E,T)$ to the experimental data for $E - E_F$ equal to 0.0010 eV is given in Figure 1. Kaneto, et. al. (11) have shown that γ-ray irradiation of

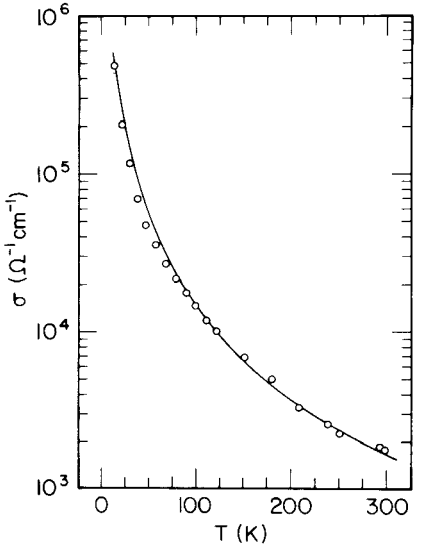

FIGURE 1. $\sigma(T)$ of $(SN)_x$ [Ref. 10] (o), and G(E,T) for $E - E_F = 0.0010$ eV (———).

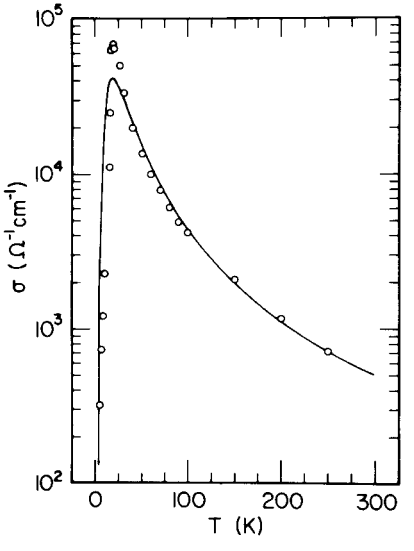

FIGURE 2. $\sigma(T)$ of $(TMTSF)_2PF_6$ [Ref. 13] (o), and G(E,T) for $E - E_F = 0.0038$eV (———).

$(SN)_x$ single crystals results in the appearance of a metal-insulator transtion in the conductivity curve. The metal-insulator conductivity maximum decreases in amplitude and shifts to higher temperatures with increasing irradiation dosage. This is the effect predicted by G(E,T) for an increase in $E - E_F$ (7).

It is known that irradiation produces defects in highly ordered single crystals. For lower quality or irradiated single crystals of $(SN)_x$ the G(E,T) function yields values of $E - E_F$ in the range $\sim 0.004 \rightarrow 0.01$ eV. As the extent of disorder is increased and polycrystalline $(SN)_x$ is formed the material becomes a semiconductor (12). The G(E,T) function describes this behavior also with $E - E_F \sim 0.01$ eV. Thus, one can associate the extent of crystal disorder in this type of material with a numerical value of $E - E_F$ obtained by use of the G(E,T) function.

The experimentally determined electrical conductivity versus temperature curves for the materials $(TMTSF)_2PF_6$ (13) and TTF-TCNQ (14), and those predicted in terms of G(E,T) for values of $E - E_F$ equal to 0.0038 and 0.012 eV, respectively, are given in Figures 2 and 3. It is well known that the amplitude of the conductivity maximum for a metal-insulator transition varies markedly from crystal to crystal for a given material. Therefore, precise fits of the G(E,T) function with experimental conductivity data for any given crystal sample are not to be expected. Lower values of $\sigma(T)_{max}$ at the metal-insulator transition temperature than those predicted in terms of G(E,T) are common, and can be expected for low quality or disordered crystals. However, the higher experimental values of $\sigma(T)_{max}$ as compared to those predicted in terms of G(E,T) that are shown for $(TMTSF)_2PF_6$ and TTF-TCNQ again raise the question of superconducting fluctuations in these materials (15).

Heeger (16) reports that deuteron irradiation, which induces crystal defects in TTF-TCNQ and similar substances, yields a decrease in the conductivity maximum and an increase in the metal-insulator transition temperature with increasing irradiation dosage. As pointed out previously these are the effects predicted by G(E,T) for in-

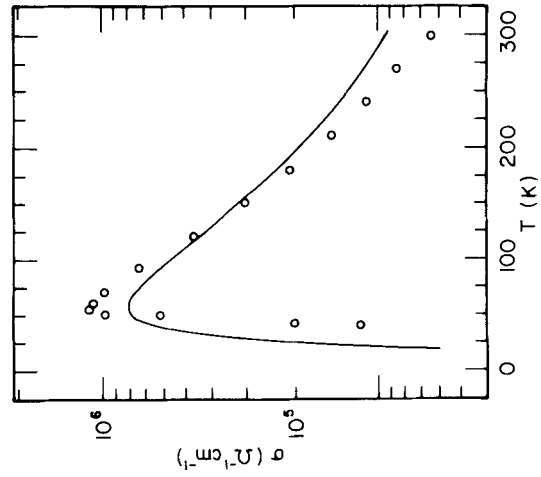

FIGURE 3. σ(T) of TTF-TCNQ [Ref. 14] (o), and G(E,T) for E - E_F = 0.012 eV (———).

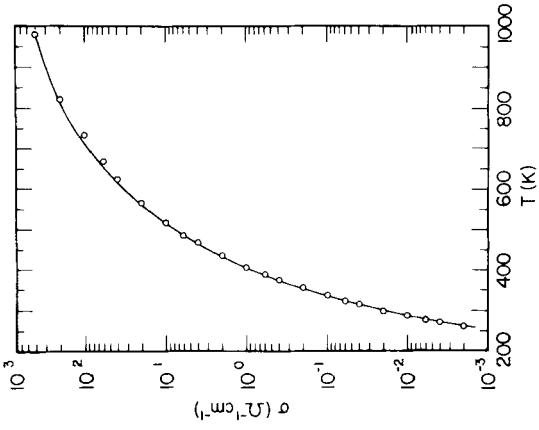

FIGURE 4. σ(T) of germanium [Ref. 17] (o), and G(E,T) for E - E_F = 0.46 eV (———).

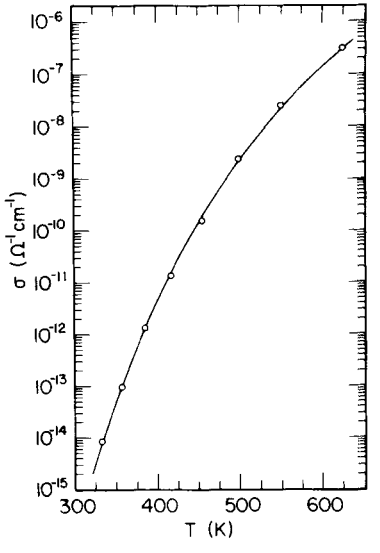

FIGURE 5. $\sigma(T)$ of Type 7740 (Pyrex) glass [Ref. 18] (o), and G(E,T) for $E - E_F$ = 1.16 eV (———).

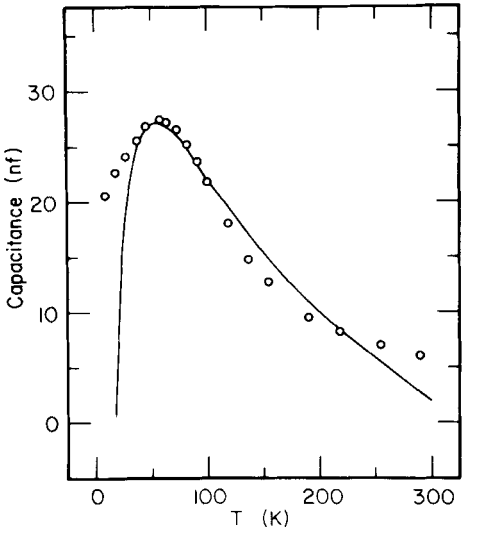

FIGURE 6. Capacitance of $SrTiO_3$ [Ref. 20] (o), and G(E,T) for $E - E_F$ = 0.010 eV (———).

creasing values of $E - E_F$. They can be expected when the extent of lattice disorder increases.

The G(E,T) function also describes the conductivity of some semiconducting materials such as single crystals of germanium (17). The experimental data for this material, and the G(E,T) function calculated with $E - E_F$ equal to 0.46 eV are given in Figure 4. The conductivity versus temperature data for vitreous type 7740 borosilicate (Pyrex) glass (18), and the curve calculated in terms of G(E,T) with $E - E_F$ equal to 1.16 eV are given in Figure 5. Even in this highly disordered material the agreement between experimental results and the G(E,T) calculations is very good. Thus, the applicability of the G(E,T) function to the temperature dependence of electrical conductivity holds for both ordered and disordered materials.

OTHER APPLICATIONS OF THE G(E,T) FUNCTION

Capacitance

The generalized electric current density, J, can be written as

$$J = J_t + J_d \qquad (5)$$

where J_t represents the transport current density, and J_d is the displacement current density. The displacement current density can be associated with the electric charge accumulation, or the capacitance (19).

Since $\sigma = J/\mathcal{E}$, where $\mathcal{E}$ is the electric field strength, one can expect the G(E,T) function to also describe the temperature dependence of the capacitance. Data for the experimental temperature dependence of the capacitance of $SrTiO_3$ (20), and the G(E,T) function with $E - E_F$ equal to 0.010 eV plotted on an arbitrary scale are shown in Figure 6.

Electromagnetic Radiation and Electrical Conductivity

The value of $E - E_F$ determined in terms of the G(E,T) function for the conductivity of $(SN)_x$ is 0.0010 eV. An energy value on the order of 0.001 eV

corresponds to electromagnetic radiation in the millimeter wavelength region. One, therefore, expects that millimeter microwave irradiation should cause anomalies in the conductivity of single crystals of materials such as high quality single crystals of $(SN)_x$. This assumes that a significant portion of the transport current density occurs within the skin depth region of the metallic substance. For metallic substances that undergo a metal-insulator transition the effect of microwave irradiation can be expected to be the most noticeable just below the electrical conductivity maximum on the low temperature side. It would be of interest if the reverse effect, microwave emission resulting from the flow of electric current, should occur.

For values of $E - E_F \sim 0.01 - 0.02$ eV the G(E,T) function describes semiconductor behavior. Energy of this order of magnitude corresponds to infrared radiation. Both microwave and infrared radiation absorption by metals and semiconductors has been studied (21). Some of these results might be reexamined in terms of the model of thermal excitation of valence electrons into the conduction band herein discussed.

Possible Relationship of G(E,T) to Superconductivity

As indicated in the Introduction the Fermi function predicts that for positive values of $E - E_F$ the conduction band electron density tends to zero. This is the result to be expected for a cumulative probability function. The G(E,T) function for values of $E - E_F < 0.001$ eV predicts significantly finite values of the conduction band electron density for temperatures near absolute zero. The G(E,T) probability density function, therefore, suggests a logical correlation between ohmic conductivity and superconductivity at temperatures near absolute zero.

CONCLUSION

Use of the derivative of the Fermi function with respect to temperature, G(E,T), as the probability density function for electron occupancy in the conduction band allows one to predict the

general form of the temperature dependence of electrical conductivity for various types of materials. A simple model of thermal excitation of valence electrons into the conduction band, and to a first approximation temperature independent mobilities and temperature independent density of states functions are assumed. The G(E,T) function is applicable to the conductivity of low-dimensional metallic substances which have a monotonic increasing conductivity with decreasing temperature, and to those that exhibit a metal-insulator transition. The G(E,T) function also describes the temperature dependence of the electrical conductivity of semiconductors such as single crystals of germanium and vitreous materials such as Pyrex glass. Collectively the range of conductivities characterized by this function span about 20 orders of magnitude and a total temperature range of approximately 1000 K.

The G(E,T) function appears to be applicable to other electron transport properties such as capacitance. The temperature dependence of the capacitance of $SrTiO_3$ is cited as an example.

Values of $E - E_F$ derived by curve fitting the G(E,T) function to experimental electrical conductivity data correspond to microwave and infrared radiation for metallic and semiconducting materials. This suggests that electromagnetic irradiation in these regions may cause anomalies in the conductivity of metals and semiconductors.

The G(E,T) function in contrast to the Fermi function predicts finite electron densities in the conduction band of metallic substances near absolute zero. This suggests a possible correlation between ohmic conductivity and superconductivity in this temperature region.

REFERENCES

1. A. J. Epstein, E. M. Conwell and J. S. Miller in Synthesis and Properties of Low-Dimensional Materials, Vol. 313, eds. J. S. Miller and A. J. Epstein (New York Academy of Sciences, New York) (1978), p. 183.
2. R. E. Peierls, Quantum Theory of Solids (Oxford University Press, London)(1974), pp. 108-12.

3. For a review see M. M. Labes, P. Love and L. F. Nichols, Chem. Rev., 79, 1 (1979).
4. R. L. Greene, G. B. Street and L. J. Sutter, Phys. Rev. Lett., 34, 577 (1975).
5. C. Hsu and M. M. Labes, J. Chem. Phys., 61, 4640 (1974).
6. A. J. Heeger in Highly Conducting One-Dimensional Solids, eds. J. T. Devreese, R. P. Evrand and V. E. vanDoren (Plenum Press, New York) (1979), p. 70.
7. P. Love, J. Phys. C: Solid State Phys., 12, L627 (1979).
8. P. Love, J. Phys. C: Solid State Phys., 16, 0000 (1983).
9. See for example J. M. Ziman, Principles of the Theory of Solids (Cambridge University Press, Cambridge)(1972), p. 136.
10. H. I. Kao, Electrical Conductivity of Polysulfur Nitride, Perylene-Iodine and Benzophenone-Iodine-Iodide Complexes, Ph.D. Thesis (Temple University, Philadelphia)(1979), p. 146.
11. K. Kaneto, K. Tanimura, K. Yoshino and Y. Inuishi, Solid State Commun., 22, 383 (1977).
12. P. L. Kronick, H. Kaye, E. F. Chapman, S. B. Mainthia and M. M. Labes, J. Chem. Phys., 36, 2235 (1962).
13. K. Bechgaard, C. S. Jacobsen, K. Mortensen, H. J. Pedersen and N. Thorup, Solid State Commun., 33, 1119 (1980).
14. A. J. Berlinsky, Contemp. Phys., 17, 331 (1976).
15. H. J. Schulz, D. Jerome, A. Mazaud and M. Ribault, J. Physique, 42, 991 (1981).
16. A. J. Heeger in Highly Conducting One-Dimensional Solids, eds. J. T. Devreese, R. P. Evrand and V. E. vanDoren (Plenum Press, New York) (1979), p. 108.
17. Adapted from F. J. Morin and J. Pm Maita, Phys. Rev., 94, 1525 (1954).
18. Adapted from Properties of Glasses and Glass-Ceramics (Corning Glass Works, Corning)(1973), p. 8.
19. N. Gauthier, Am. J. Phys., 51, 168 (1983).
20. Courtesy D. J. Bartos, Cryogenic Temperature

Sensing Elements (Lake Shore Cryotronics, Inc., Westerville, Ohio)(1976), p. 4.
21. See for example a) V. M. Fomin and E. P. Pokatilov, Phys. Stat. Sol. B, 114, 615 (1982), b) R. Fastampa, M. Giura and R. Marcon, Solid State Commun., 45, 1025 (1983), and c) K. Shimakawa, Phil. Mag. B, 48, 77 (1983).