

# Electrical transport properties of $\text{Eu}_2\text{Ti}_2\text{O}_7$ single crystal

A. K. PANDIT, T. H. ANSARI, R. S. SINGH, R. A. SINGH  
*Department of Physics, University of Gorakhpur, Gorakhpur 273 009, India*

B. M. WANKLYN  
*Clarendon Laboratory, Department of Physics, University of Oxford, Oxford, UK*

The electrical conductivity, thermoelectric power and dielectric constant of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  single crystal have been studied in the temperature range 300–1000 K.  $\text{Eu}_2\text{Ti}_2\text{O}_7$  is found to be a n-type semiconductor with energy band gap of 2.5 eV. The compound exhibits an extrinsic nature upto 700 K and intrinsic nature above 700 K. Thermoelectric power decreases with temperature in the region 300–700 K whereas it increases with temperature in the region 700–1000 K. Dielectric constant increases with temperature in the entire temperature range studied with a discontinuity at  $T \sim 700$  K.

## 1. Introduction

Europium titanate,  $\text{Eu}_2\text{Ti}_2\text{O}_7$ , is one of the isomorphous family of compounds with the general formula  $\text{Ln}_2\text{Ti}_2\text{O}_7$ , where Ln is a rare-earth. Of the rare-earth titanates only the compounds included between samarium and lutetium possess the pyrochlore structure because of the value of the ionic radius of the trivalent cation.  $\text{Eu}_2\text{Ti}_2\text{O}_7$  has a pyrochlorine-type structure (Fd3m). The cubic unit cell has a size of  $\approx 1.02$  nm on a side and contains 8 formula units, i.e. 88 atoms [1, 2]. Only the crystallographic properties of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  have been studied till now. This paper reports our investigations on the electrical transport properties of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  single crystal in the temperature range 300–1000 K.

## 2. Experimental procedure

Single crystals of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  were grown by the flux method at the Clarendon Laboratory Oxford, UK. Details about the crystal growth and identification techniques are given elsewhere [3]. The crystal on which the measurements were carried out, has a dimension 5.95 mm  $\times$  2.77 mm  $\times$  2.63 mm. Direct current (d.c.) electrical conductivity and thermoelectric power have been measured with the help of a digital multimeter (PM 2522/90, Philips, India) with an accuracy better than  $\pm 0.25\%$  and  $\pm 0.20\%$  for resistance and electromotive force (e.m.f.) measurements, respectively. Alternate current (a.c.) electrical conductivity and dielectric constant have been determined using an autocomputing digital LCR-Q meter (4910, Applied Electronics Ltd, Thane, India) at an internal frequency of 1 kHz. For dielectric measurement, the crystal was used as a dielectric medium. For all the measurements perpendicular to *c*-axis, the two probe method was employed. Due to the small size of the crystal, the measurements parallel to the *c*-axis were

not possible. Platinum foils and silver paint were used as electrode materials. Temperatures are recorded with the help of chromel-alumel thermocouple attached to the platinum electrodes. The details regarding the sample holder assembly and measuring techniques are given elsewhere [4].

## 3. Results and discussion

Variation of the logarithms of a.c. and d.c. electrical conductivities ( $\log \sigma_{\text{a.c.}}$  and  $\log \sigma_{\text{d.c.}}$ ) with absolute temperature ( $10^3/T$ ) are shown in Fig. 1. The conductivities follow an exponential relation [5] for semiconductors

$$\sigma = \sigma_0(T) \exp(-W/kT) \quad (1)$$

where

$$\sigma_0(T) = 2\epsilon(2\pi kT/h^2)^{3/2} (m_e m_h)^{3/4} (\mu_e + \mu_h) \quad (2)$$

with two different slopes in the temperature ranges, namely, 300–700 K and 700–1000 K. Here  $(\mu_e + \mu_h)$  varies with temperature as  $T^{-3/2}$ , making  $\sigma_0(T)$  constant.  $W$  is the activation energy;  $m_e$ ,  $\mu_e$  and  $m_h$ ,  $\mu_h$  are effective masses and mobilities of electrons and holes, respectively, and the other symbols have their usual meanings. Variation of electrical conductivity with temperature indicates that  $\text{Eu}_2\text{Ti}_2\text{O}_7$  is a semiconductor. The activation energies and  $\sigma_0(T)$  have been calculated from the slopes and intercepts of  $\log \sigma_{\text{d.c.}}$  versus  $10^3/T$  plot, respectively. The electrical transport parameters, activation energy,  $W$ , and  $\sigma_0(T)$  in the two temperature regions have been tabulated in Table I.

In a semiconducting material, the electrical conduction at low temperatures is always associated with impurities, defects and interstitials, etc. which are generally present in the forbidden energy gap of the material and lowers the value of activation energy to a greater extent. The low value of activation energy,

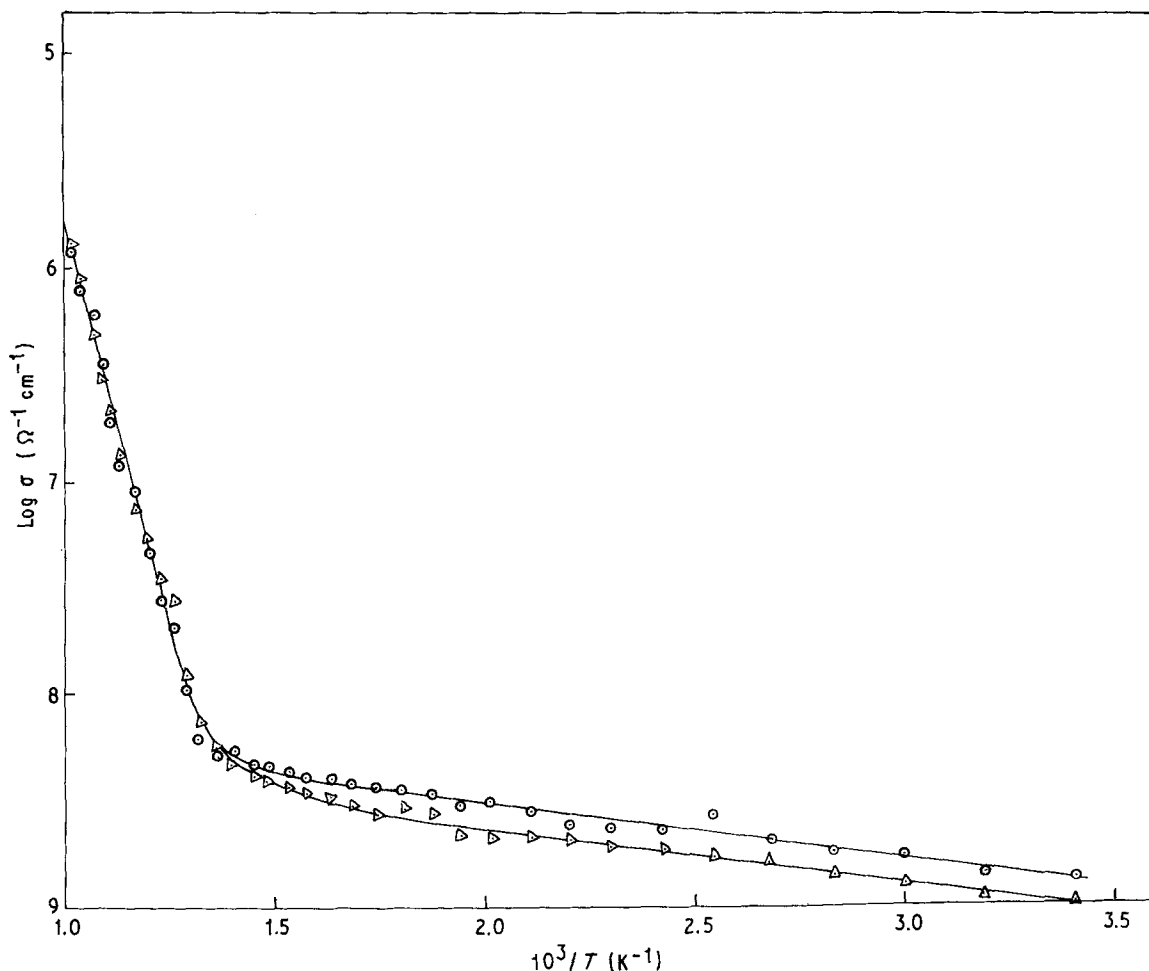


Figure 1 Variation of logarithms of a.c. and d.c. electrical conductivities ( $\log \sigma_{a.c.}$  and  $\log \sigma_{d.c.}$ ) with reciprocal of absolute temperature ( $10^3/T$ ): (○) a.c. conductivity and, (△) d.c. conductivity.

TABLE I Electrical transport parameters of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  single crystal

Temperature range (K)	Activation energy (eV)	$\sigma_0(T)$ ( $\Omega^{-1} \text{cm}^{-1}$ )
300–700	0.18	$8.61 \times 10^{-7}$
700–1000	1.25	3.91

$W = 0.18$  eV and the charge carrier mobility  $4.61 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ , calculated from the electrical conductivity and thermoelectric power measurements, suggest extrinsic conduction in  $\text{Eu}_2\text{Ti}_2\text{O}_7$  below 700 K. The low value of charge carrier mobility indicates localization of the charge carriers due to interaction of impurity charge carriers with the lattice sites. The ionic nature of the compound and the presence of the narrow 4f band in  $\text{Eu}_2\text{Ti}_2\text{O}_7$  facilitate the interaction of the charge carriers with the lattice sites. All these circumstances lead to small polaron formation. The small polaron motion in an ionic compound occurs by two distinct mechanisms, namely, small polaron band conduction mechanism and small polaron hopping conduction mechanism. In the case of small polaron band conduction, the mobility of the charge carriers decreases with increase in temperature but in the case of small polaron hopping conduction the mobility increases exponentially with temperature. In this compound it is observed that the mobility of

the charge carriers decreases with temperature as also indicated by the decrease in the thermoelectric power below  $T \sim 700$  K. In the low temperature band-motion region, the drift mobility is mainly determined by the phonon scattering and hence it decreases with temperature. Therefore, a decrease in thermoelectric power with temperature, which is due to decrease in the mobility of the charge carriers, is taken as confirmation of small polaron band conduction in the temperature range 300–700 K. However conductivity due to ionized impurity centres is also probable because small polaron band conduction will not take place in the temperature region 300–700 K [6]. The conduction due to ionized impurity centre can be explained in terms of donors or acceptors and is represented by the expression [7]

$$\sigma_d = A \exp(-E_i/kT) \quad (3)$$

where  $E_i$  is the ionization energy of donors or acceptors and usually  $E_i \sim 0.1$  eV for semiconducting materials. The activation energy found below 700 K is comparable to this ionization energy. Therefore it is concluded that in  $\text{Eu}_2\text{Ti}_2\text{O}_7$  the electrical conduction is certainly due to ionized impurity centres.

The activation energy of 1.25 eV estimated in the higher temperature range, 700–1000 K, seems to be an intrinsic activation energy as most of the impurity charge carriers will be exhausted upto this temperature. So, the change in the nature of the  $\log \sigma$  versus

$10^3/T$  curve at  $T \sim 700$  K is due to the change in the conduction mechanism, i.e. transition from extrinsic to intrinsic conduction. However it may also be due to other transitions like magnetic or phase transition which have not been studied till now. To understand the electrical conduction mechanism in a material, it is necessary to have an idea of the electronic energy bands available for the electrical transport. The relevant bands for conduction in this solid are  $O^{2-}$ : 2p filled;  $Eu^{3+}$ : 4f partially filled;  $Ti^{4+}$ : 3d and  $Eu^{3+}$ : 5d empty bands. The only partially filled band expected in this solid is the 4f band, but it has been shown that 4f electrons have almost atomic character even in rare-earth solids, and form only very narrow and highly correlated bands [8, 9]. The value usually quoted for bandwidth is 0.05 eV. Hence the participation of 4f electrons in the conduction process is improbable [10, 11]. The 5d band in rare-earth solids is regarded as the conduction band [9]. Thus it seems likely that electrons in the 5d band, caused by the thermal excitation of electrons from 4f or 5p bands and holes left thereby are responsible for electrical conduction above  $T \sim 700$  K. So only appropriate bands for high mobility electrical conduction are  $Eu^{3+}$ : 5d empty band and  $O^{2-}$ : 2p filled band. The 2p band is expected to be an ordinary band (about 4 eV wide) and the large polaron theory of conduction should be applied in this band. The 5d band is in comparison a narrow band, the mobility of charge carriers in the 5d band is thus expected to lower by comparison with the mobility of charge carriers in  $O^{2-}$ : 2p band. Thus intrinsic conductivity should be dominated by large polarons. The electron or hole current domination will depend on

the effective mass of the charge carriers in the empty band  $Eu^{3+}$ : 5d and filled band  $O^{2-}$ : 2p [12, 13]. However, both these holes and electrons are expected to interact with the lattice and this may lead to the formation of large polarons as discussed by several authors [14–16]. The electrical conduction of a large polaron is of band type and the expression for the conductivity is

$$\sigma = \sigma_0 \exp(-E_g/2kT) \quad (4)$$

where  $E_g$  is the energy band gap of the solid and  $\sigma_0$  is a constant. In the temperature range 700–1000 K,  $\log \sigma$  versus  $10^3/T$  curve is a straight line and conduction is probably band type due to large polarons. From this part of the curve one gets an energy band gap of  $E_g = 2.5$  eV and  $\sigma_0 = 3.91 \Omega^{-1} \text{cm}^{-1}$ .

It is seen from Fig. 1 that in the temperature range 300–700 K, a.c. conductivity is slightly higher than d.c. conductivity which predicts that the conductivity in this temperature region is ionic as well as electronic. Coincidence of the a.c. and d.c. conductivities at higher temperatures show that the material is predominantly an electronic semiconductor. Thermoelectric power,  $S$ , was calculated using the relation

$$S = \lim_{\Delta T \rightarrow 0} \frac{\Delta E}{\Delta T} \quad (5)$$

where  $\Delta E$  is the thermo e.m.f. generated across the crystal due to temperature difference  $\Delta T$ . The plot of  $S$  versus  $10^3/T$  is shown in Fig. 2. It is observed that  $S$ , first decreases with temperature, attains a minimum around 700 K and then starts increasing with temperature. Negative values of  $S$  over the entire temperature

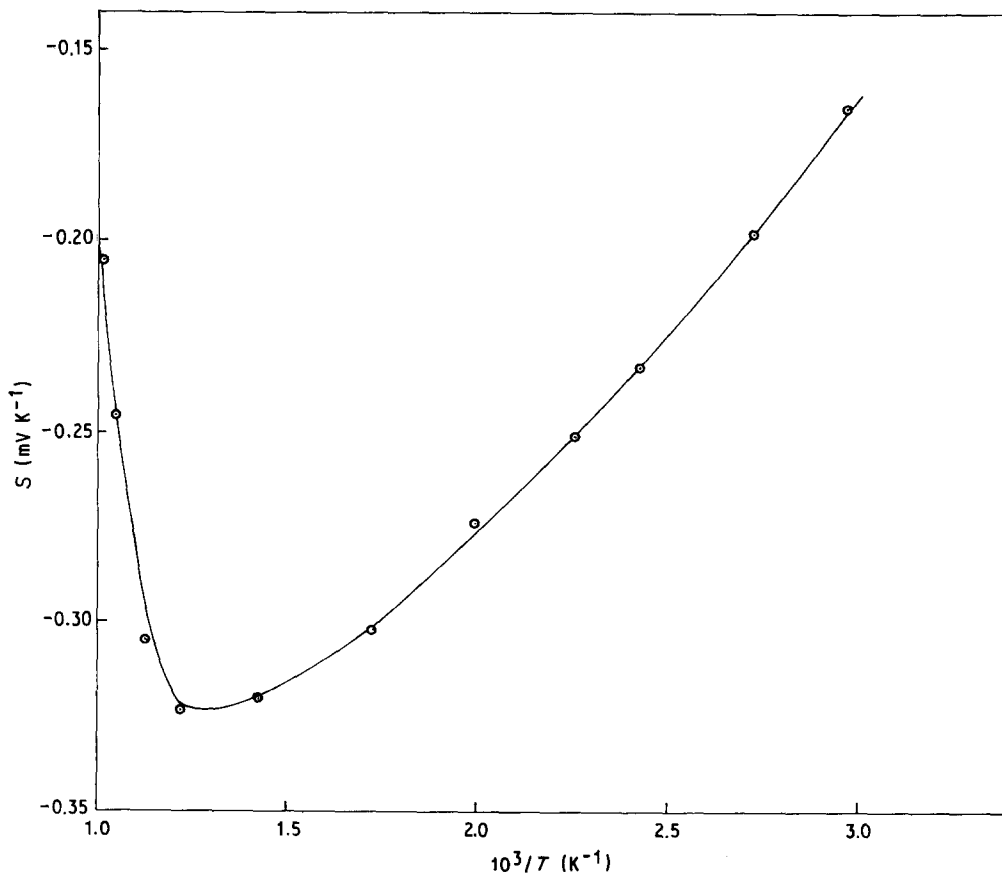


Figure 2 Variation of thermoelectric power ( $S$ ) with reciprocal of absolute temperature ( $10^3/T$ ).

range, indicate that  $\text{Eu}_2\text{Ti}_2\text{O}_7$  is a n-type semiconductor. According to a two-band model the variation of  $S$  with temperature is given by [17]

$$S = \frac{\eta}{T} + K \quad (6)$$

where

$$\eta = -\frac{E_g}{2e} \left( \frac{c-1}{c+1} \right) \quad (7)$$

$$K = -\left[ \frac{2k}{e} \left( \frac{c-1}{c+1} \right) + \frac{3k}{4e} \log_e(a) \right] \quad (8)$$

$$c = \frac{\mu_e}{\mu_h} \quad \text{and} \quad a = \frac{m_e}{m_h}$$

Here  $E_g$  is the energy band gap and the other symbols have their usual meanings. From the slope and intercept of  $S(T)$  in Fig. 2, and using Equation 6,  $\eta$  and  $K$  have been determined. By using Equations 7 and 8 we have calculated the values of  $c$  and  $a$  along with  $\sigma_0(T)$  given by Equation 2, the value of charge carrier mobility was deduced to be  $4.61 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  in the temperature range 300–700 K. In the low temperature region (300–700 K), thermoelectric power decreases with temperature which is due to a decrease in mobility of the charge carriers.

In the temperature range 700–1000 K, there is only the possibility of large polaron conduction because the small polaron conduction is always associated with impurity conduction and upto this temperature all the impurity charge carriers will be exhausted. The

large polaron band conduction takes place via normal band mechanism with the enhanced mass of the charge carriers. According to this mechanism, mobility of the charge carriers should decrease with increasing temperature which ultimately leads to a decrease in thermoelectric power with increasing temperature. In the present case while electrical conduction seems to be due to large polarons, it is increasing with increase in temperature. This abnormal behaviour may be most probably due to the onset of ionic conduction at higher temperature.

The dielectric constant,  $\epsilon'$ , of  $\text{Eu}_2\text{Ti}_2\text{O}_7$  has been estimated in the temperature range 300–1000 K using the relation [18]

$$\epsilon' = 11.3 Ct/A \quad (9)$$

where  $C$  is the capacitance (picofarads),  $t$  is the thickness of the crystal (cm) and  $A$  is the surface area of the electrode ( $\text{cm}^2$ ). Variation of  $\log \epsilon'$  with temperature,  $T$ , is shown in Fig. 3. The trend of the variation of dielectric constant,  $\epsilon'$ , with temperature is similar to that of the electrical conductivity, with a discontinuity at  $T \sim 700$  K. The slow variation of  $\epsilon'$  at low temperatures is due to the ionic nature of the compound and the discontinuity at 700 K is due to change in the conduction mechanisms. An increase in the ionic distance due to temperature, influences the ionic and electronic polarizations. This happens because the lattice expands and polarizability of the ions is affected by the change in temperature and available volume

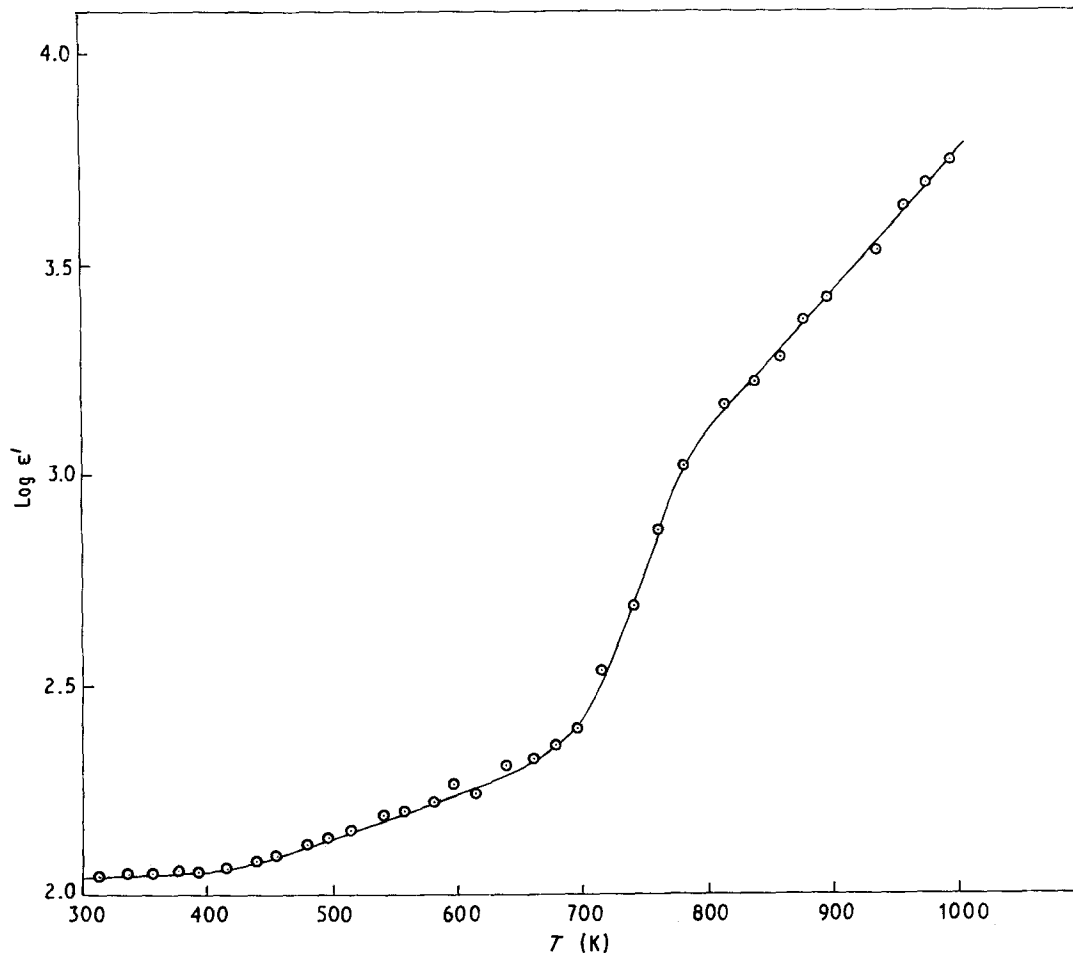


Figure 3 Variation of dielectric constant ( $\epsilon'$ ) with absolute temperature ( $T$ ).

[19]. Rapid increase of the dielectric constant above 700 K is probably due to the onset of ionic conduction in which the number of charge carriers increases exponentially and produces high space charge polarization, which largely contributes to dielectric constant.

### Acknowledgement

One of the authors (THA) thanks CSIR (India) for awarding the SRF.

### References

1. M. P. VAN DIJK, J. H. H. TERMAAT, G. ROELOFS, H. BOSCH, G. M. H. VAN DE VELDE, P. J. GELLINGS and A. J. BURGGRAAF, *Mat. Res. Bull.* **19** (1984) 1149.
2. M. FAUCHER and P. CARO, *J. Solid State Chem.* **12** (1975) 1.
3. B. M. WANKLYN, *J. Mater. Sci.* **7** (1972) 813.
4. Y. P. YADAVA and R. A. SINGH, *Mater. Chem. Phys.* **17** (1987) 259.
5. T. C. HERMANN and J. M. HONING, in "Thermoelectric power and Thermomagnetic Effects and Applications" (McGraw-Hill, New York, 1976) p. 142.
6. I. K. NAIK and T. Y. TIEN, *J. Phys. Chem. Solids* **39** (1978) 311.
7. A. J. DEKKER, in "Solid State Physics" (MacMillan, London, 1964) p. 305.
8. B. CONQUILIN and A. BLANDIN, *Adv. Phys.* **17** (1968) 281.
9. C. E. T. GONCALVES DA SILVA and L. M. FALICOV, *J. Phys. C: Solid State Phys.* **5** (1972) 63.
10. Y. A. ROCHER, *Adv. Phys.* **11** (1962) 233.
11. R. RAMIREZ and L. M. FALICOV, *Phys. Rev.* **13** (1971) 2425.
12. J. M. ZIMAN, in "Principles of the theory of solids" (Cambridge University Press, UK, 1964) p. 179.
13. C. KITTEL, in "Introduction to Solid State Physics" (Wiley, New York, 1971) p. 361.
14. H. FROHLICH, *Adv. Phys.* **3** (1954) 325.
15. G. R. ALLCOCK, *ibid.* **5** (1956) 412.
16. J. APPEL, in "Solid State Physics." (Academic Press, New York, 1968) p. 193.
17. O. G. PALANNA, A. L. SHASHI MOHAN, A. B. BISWAS, *Proc. Indian Acad. Sci.* **86A** (1977) 455.
18. J. P. SUCHET, in "Electrical Conduction in Solid Materials" (Pergamon Press, Oxford, 1975) p. 47.
19. C. P. SMYTH, in "Dielectric Behaviour and Structure" (McGraw-Hill, New York, 1955) p. 132.

*Received 4 April  
and accepted 30 July 1991*