

CHAPTER IV

ELECTRICAL CONDUCTIVITY

Electrical Conductivity

4.1 Introduction

The ferrites are oxide magnetic materials with their resistivity lying between $10^{-3} \Omega \text{ cm}$ and $10^{11} \Omega \text{ cm}$. The high resistivity of ferrites makes them suitable over metals, in high frequency applications. Secondly the eddy current losses are also less. It has been well established that the electrical properties of polycrystalline ferrites can be varied over a wide range through the heat treatment given to them at the time of preparation. In Fe_3O_4 the low resistivity is observed due to the presence of Fe^{2+} and Fe^{3+} ions in the crystallographically equivalent positions¹. Like other semiconducting oxides, the resistivities of ferrites is greatly affected by the presence of impurities. According to VerWay and de Boer² efficient electronic conduction in these compounds can be associated with the presence of ions of a given element in more than one valance state. Secondly, VerWay *et al.*,¹ have shown that conduction can be enhanced in high resistive oxides by incorporating very small amount of foreign oxides into the structure whose metal ions take valancies other than that of host metals. Van Uitert³ has shown that the resistivity of Nickel and Magnesium ferrite can be varied by constitution of manganese and cobalt. Apart from these contribution

resistivity of materials also comes from cation distribution, crystal structure, porosity, grain size, impurity inclusions, chemical and oxidation states and other unknown and known scattering mechanisms.

In this chapter the conduction mechanisms in oxides and ferrites are briefly discussed. The explanations of the results on the temperature dependent upon measurements of resistivity is presented at the end.

4.2 Conduction Mechanism

The oxide crystal structure may be conveniently described in terms of lattice of oxygen ions, with relatively small metal ions occupying the interstitial positions. Due to the predominantly ionic ~~bonding~~ character of metal oxides, the electrical conductivity is mainly decided by the electrons with 3d like wave functions, the outer electronic configuration of O^{2-} being stable. However the satisfactory calculations of the eigenvalues of these functions remains a problem of great difficulty in solid state physics. Evaluation of a realistic energy level scheme must therefore take help of the simplified theoretical models based on empirical rules. As far as the electrical properties of oxides are concerned the models are successful only in providing the semi-quantitative explanations of experimentally established results. Never the less these concepts are very useful for discussing the electrical conduction in solids. Energy levels schemes in solids can be had on the

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basis of any one of the two extreme initial postulates viz. the nearly free electron model and the tight bonding approximation. In the former the electrons have been assumed to move throughout the solid and interaction of particles is treated as a small perturbation and in the latter it has been assumed that the solids consists of an array of atoms and interaction may be treated as a small perturbations of the properties of the free atom.

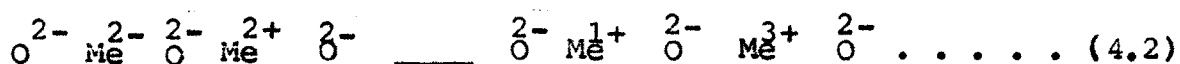
In the element of first transition series, the 3d levels are being systematically filled from Sc to Ni. In the crystalline field of solid the levels are split into a triplet and doublet. The triplet or t_{2g} states lies below doublet or e_g states in oxides with rock salt structure. These oxides then be expected to be metallic conductor at least above the antiferrimagnetic disorder temperature⁵. Below the Neel temperature exchang forces could give rise to further splitting of 3d band. The oxides however behaves as semiconductors at all temperatures and have intrinsic activation energies far in excess of those which could be accounted for by exchange splitting. It is evident from that this descriptions in terms of conventional band theory fail to account for the electrical transport properties. The failure has its origin in the low mobility of electrons in the 3d band.

4.2.a Conduction in oxides

The majority of the transition metal oxides are also semiconductors and their electrical conductivity may be described by an equation.

$$\sigma = \frac{A}{T^{B-1}} \text{Exp} (- B/KT) \dots \dots \dots (4.1)$$

where B is 1 or 2 and A and B are constants. The activation energy ranges upto about 1.5 ev, though very much smaller values are encountered at sufficiently low temperatures. For an oxide of composition MeO the activation of a conduction electron may be represented by



The energy needed for the relation of ion pairs Me^{3+} and Me^{1+} corresponds to a gap in the density of states. The following terms are considered to be contributing to the activation energy which arises from an electron correlation effect.

- i) The difference between ionisation energy and the electron affinity of the free Me^{2+} ion.
- ii) The difference in Madelung energy of the two configurations shown in eqn. (4.2).



iii) The difference in crystal field stabilization of the above configurations.

iv) Energies of the polarization of the surrounding crystal lattice.

The terms (i) and (ii) are of opposite sign and are dominant (10 - 50 eV) while (iii) will not normally exceed one or two eV, (iv) may be of the order of a few eV. Somewhat similar considerations may also be applied to obtain an estimation of the activation energy needed for impurity conduction. The polarization term (iv) can have an important effect on the mobility of charge carriers and also upon the electrons and holes which are loosely bound to the impurity centres. The polaron theory used to describe the motion of electrons and holes moving through the solid in a potential well created by their polarizing the surrounding medium is developed during the last few years and the same is discussed here briefly.

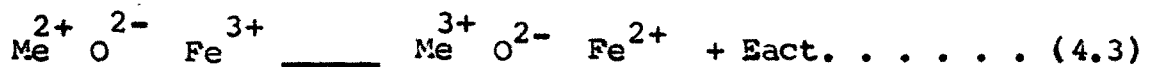
4.2 b Mixed valencies and controlled valency semiconductors

A relatively good conductivity in ionic compounds with an appreciable concentration of metal ions in two valence states was first investigated by de Boer and VerWay⁴ for magnetite. Magnetite has $\frac{1}{3}$ of metal ions in tetrahedral sites and $\frac{2}{3}$ on octahedral sites. The octahedral site contain equal number

of Fe^{2+} and Fe^{3+} which are randomly distributed above a disorder temperature 119 K. Charge transport occurs by transfer of electrons between otherwise trivalent iron ions. The process differs from one represented in equation (4.2) and energy term(iv) polarisation effect is only present. The overlap between the 3d like wave functions of nearest neighbour cations is sufficient to give rise to almost metallic type of conduction.

4.2. c Conduction in Ferrites

This above mechanism of electron transport does not apply to other simple ferrites where all Fe ions are trivalent. Transport may then be represented by



where Eact., the activation energy may reflect the difference between the third ionisation potential of Fe^{3+} and Me^{3+} ions in the solid. Jonker⁶ has studied the ferrite $Co_x Fe_{3-x} O_4$ and predicted quantitatively the mechanism stated above.

Ionic state of the cations in ionic crystal gives some insight into the effect of impurities on electrical properties. In so far as the ionisation potential of O^{2-} ion is the dominant term. Substitution upto 1% or so of the cations of another element of same valancy should have little effect upon unductivity.

If the dopant has higher valency it will contribute donor centres; it has lower valency it will provide acceptor centres.

Analogous considerations may also apply to cations of mixed valency in ferrites which result from a departure from the ideal metal to oxygen ratio. A cation vacancy in monoxide crystal will lead to the creation of two positive holes in the 3d energy band. Conversely an oxygen ion vacancy will contribute two extra charges are detached from their vacancies by thermal agitation n-type conductivity is induced in oxygen deficient and p-type conductivity in oxygen excess materials. Some oxides are very difficult to prepare homogeneously with stoichiometric anion to cation ratio. Extrinsic semiconduction may then prevail throughout the temperature region amenable to electrical measurements. In such cases it may still be possible to infer the activation energy of intrinsic conduction from samples from which extrinsic effects have been suppressed by introduction of compensating impurities. This was demonstrated by Van Uiter⁷ in $\text{Ni Fe}_2\text{O}_4$ by replacing 1 to 2% Fe by Mn or Co. Electrons donated by oxygen vacancies will fill the impurity levels in preference to iron conduction levels. Mixed vacancy state will be confined to the impurity element if its local concentration exceeds twice that of oxygen vacancies. This technique is based on the assumption that the impurity band conduction is absent and the allowed impurity concentrations indicate that the cation wave functions do not extend significantly beyond nearest neighbour distance in the B lattice. Electrons and holes are

known to move by thermally activated hopping mechanism except for pseudometallic composition region close to magnetite.

Elwell et al.,⁸ have calculated intrinsic consideration to materials which have been prepared under different conditions of oxidation.

4.3 Electron Hopping and Polarons

As is pointed out earlier the conventional band theory fails to predict the semiconductivity for transition metal monoxides which are essentially ionic in character. Secondly the Bloch type wave functions are also not appropriate for the description of electrons which are almost fully localized on the specific cations.

Another correlation may also play a role in determining the mechanism of charge transport. The electrostatic interaction between a conduction electron or hole and nearby ions may result in a displacement of the latter and hence in polarisation of the surrounding region. So the carrier becomes situated at the centre of the polarisation potential well. If this well is deep enough a carrier may be trapped at a lattice site and its translation to a neighbouring site may be determined by thermal activation. This has been described hopping mechanism. That electron takes part in a diffusion process by jumps from one lattice site to another. The thermal activation process is encountered in ionic diffusion and ionic conductivity. The following expression for mobility⁹ of a charge carrier can be written.

$$\mu = \frac{e^2 d^2 \omega_0}{kT} \exp\left(\frac{-q}{kT}\right) \dots \dots \dots (4.4)$$

where, d = distance between nearest neighbours,

ω_0 = frequency of vibration,

q = activation energy for hopping process.

This has been used by many authors in discussion of conductivity. With the development of polaron theory it has become evident that equation (4.4) represents a special case of much more complicated relationship between mobility μ and a parameter of ionic lattice.

For realistic model for the calculation of mobility a knowledge of approximate spatial extent of potential well is required. If the potential well extends over many lattice units in the crystal, the excess charge may be considered to interact with a dielectric continuum and this model has been employed by Frohlich¹⁰ to formulation interaction Hamiltonian for 'large' polarons. He gave the parameter known as electron phonon coupling constant for discussion of polarons. The coupling constant is defined by him as

$$\alpha = \frac{e^2}{\hbar} \left\{ 2 \frac{m^*}{\hbar} \omega_0 \right\}^{1/2} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_0} \right) \dots \dots \dots (4.5)$$

where m^* is the effective mass of the carrier in the lattice and ϵ_0 and ϵ_{∞} are the dielectric constant of the surrounding environment and high frequency dielectric constant respectively.

The characteristics of the polaron are determined by the coupling constant and by the conduction levels of the rigid lattice. For small polarons the well is confined to a volume comparable to the ionic volume. It is self evident that for small polaron the interaction between the individual near neighbour ions is important. The actual polaron size can be informed from consideration of the free energy small polaron formulation is favoured in solids which combine a large coupling constant with a narrow conduction band.

At sufficiently low temperature a small polaron should behave as a particle moving in a very narrow band. At high temperatures small polaron motion may result from the absorption of one or more phonons and this process is essentially the hopping mechanism. To a good approximation the contribution from conventional band mobility and from the hopping mechanism are additive. If the time of tunnelling of the excess charge from one ion to the next is less than the time τ between successive hopping transitions, small polarons conduction will be dominant transport mechanism. There is strong experimental evidence for the existance of small polarons and for the hopping process¹¹.

4.4 Conductivity and Thermoelectric Power

4.4.a Conductivity

Imperfection in lattice will result in a spectrum of donor and acceptor levels within the energy gap. Total number of such levels may be very small compared to N_0 , where N_0 are metal ions and have lattice effect on electrical conductivity in the intrinsic region, but affect the low temperature properties. It is general feature of semiconductors as sufficiently low temperatures the electrical transport properties have a complicated dependence on T which is determined by structural defects and impurities.

The conductivity can then be written as

$$\sigma = e (n \mu_1 + p \mu_2) \dots \dots \dots (4.6)$$

where μ_1 and μ_2 are mobilities of electrons and holes, n and p are concentration of mobile electron and hole.

Activation energy does not provide much insight into the mechanism of charge transport, because the dominant temperature dependent term of both hopping mechanism and of the activation of electrons into the conduction levels are of the same form as eqn (4.1) indistinguishable included in the activation energy found out experimentally.

4.4. b Thermoelectric power

Studies on thermoelectric power provide a method to separate the contributions to activation energy E in the expression (4.7)

$$\sigma = \frac{B}{T \exp \left(\frac{q_1 + q_2 + E}{KT} \right)} \dots \dots \dots (4.7)$$

For the electrical conductivity assuming the schematic band structure model¹² for the oxide semiconductors, the phenomenological relation between the peltier coefficient and seebeck coefficient together with the equation of electrical conductivity in terms of carrier concentration and their mobility gives the relations.

$$e\alpha = -K \ln \left(N_0^A / n \right) \dots \dots \dots \text{for n-type} \dots \dots \dots (4.8)$$

$$e\alpha = +K \ln \left(N_0^A / p \right) \dots \dots \dots \text{for p-type} \dots \dots \dots (4.9)$$

such a study establishes the density of charge carrier and their average mobility together with the electrical conductivity measurements.

Results and Discussion

The present results on the measurement of d.c. resistivity of some hexagonal ferrites as a function of temperature are plotted

in figs. 4.1 - 4.12. The arrow on the plots indicates the temperature (T_c) at which the slope of the $\log \rho$ versus

$\frac{1}{T}$ curves changes its value. The measurements on resistivity

were carried out in the temperature region 20°C to 650°C .

The activation energies, ΔE , in the region both above and below T_c , calculated by using the standard exponential relation viz. $\rho = C \exp(\Delta E/KT)$ between resistivity and temperature for ferrites, are tabulated in the Table 4.1. The observed values of curie temperatures and the values of curie temperatures reported earlier for some ferrite samples, along with the values of interaction energy are also given in the same table.

The plots of $\log \rho$ Vs $\frac{1}{T}$ are linear and as the temperature increases (lower values of $\frac{1}{T}$) the resistivity decreases. This is characteristic of the semiconducting behaviour of ferrites under study. This form of relationship is indeed often observed for many ferrites having spinel^{13,14} and garnet structure¹⁵. The change in the slope of $\log \rho$ Vs $\frac{1}{T}$ plot, indicates a magnetic transition. The temperature at which break occurs, corresponds closely to the observed ferromagnetic curie temperature for the ferrite.

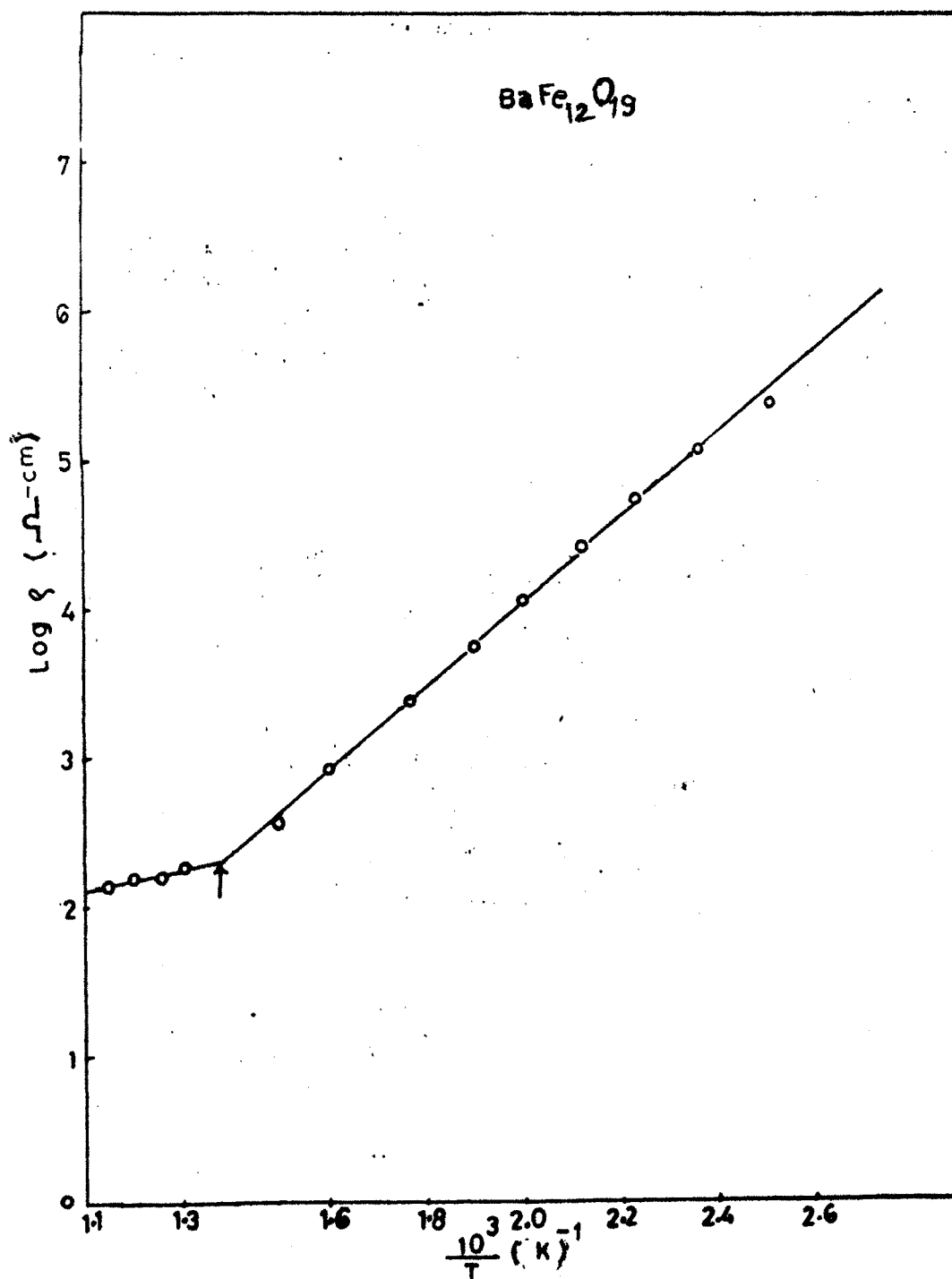


Fig. 4.1

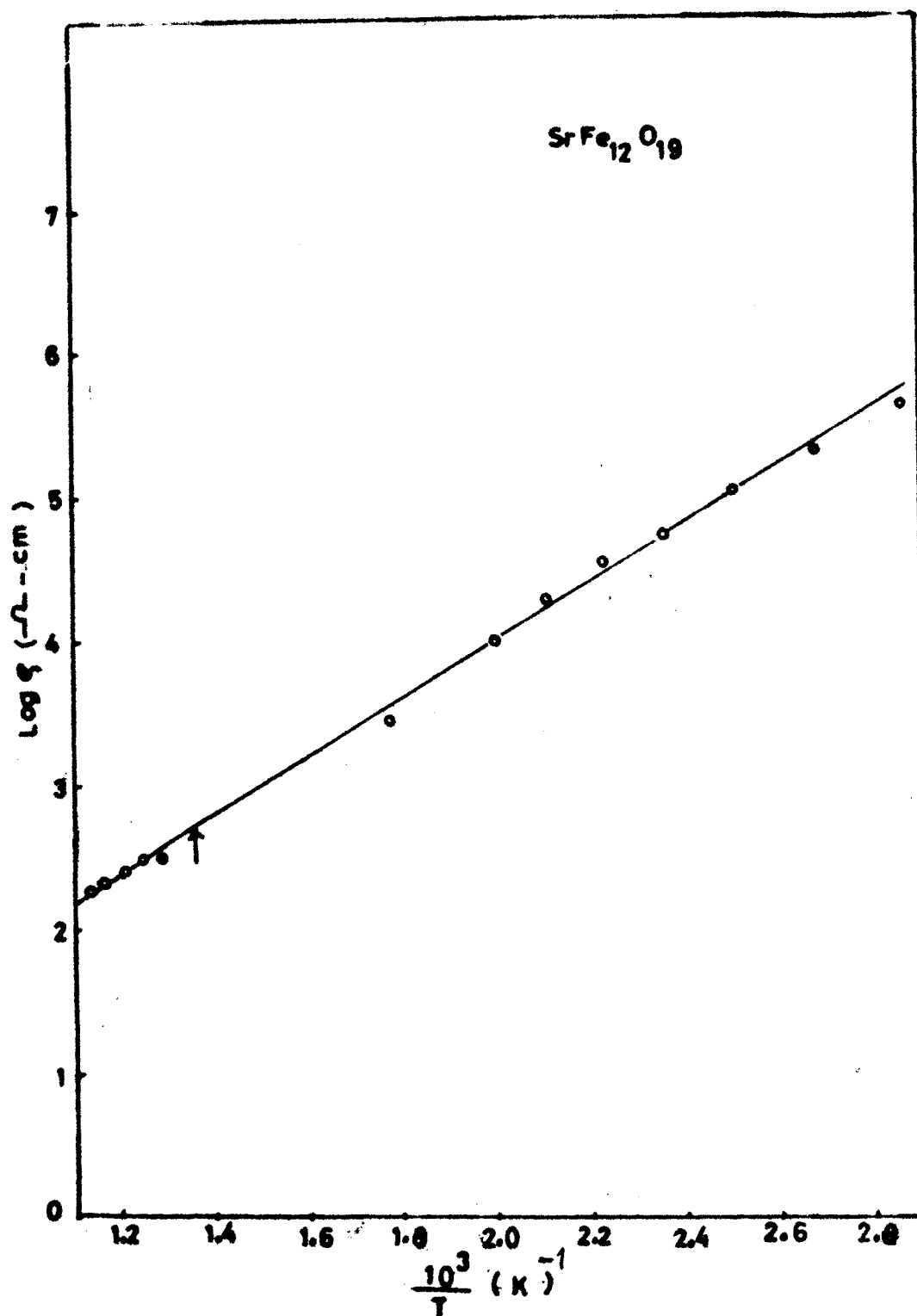


Fig. 42

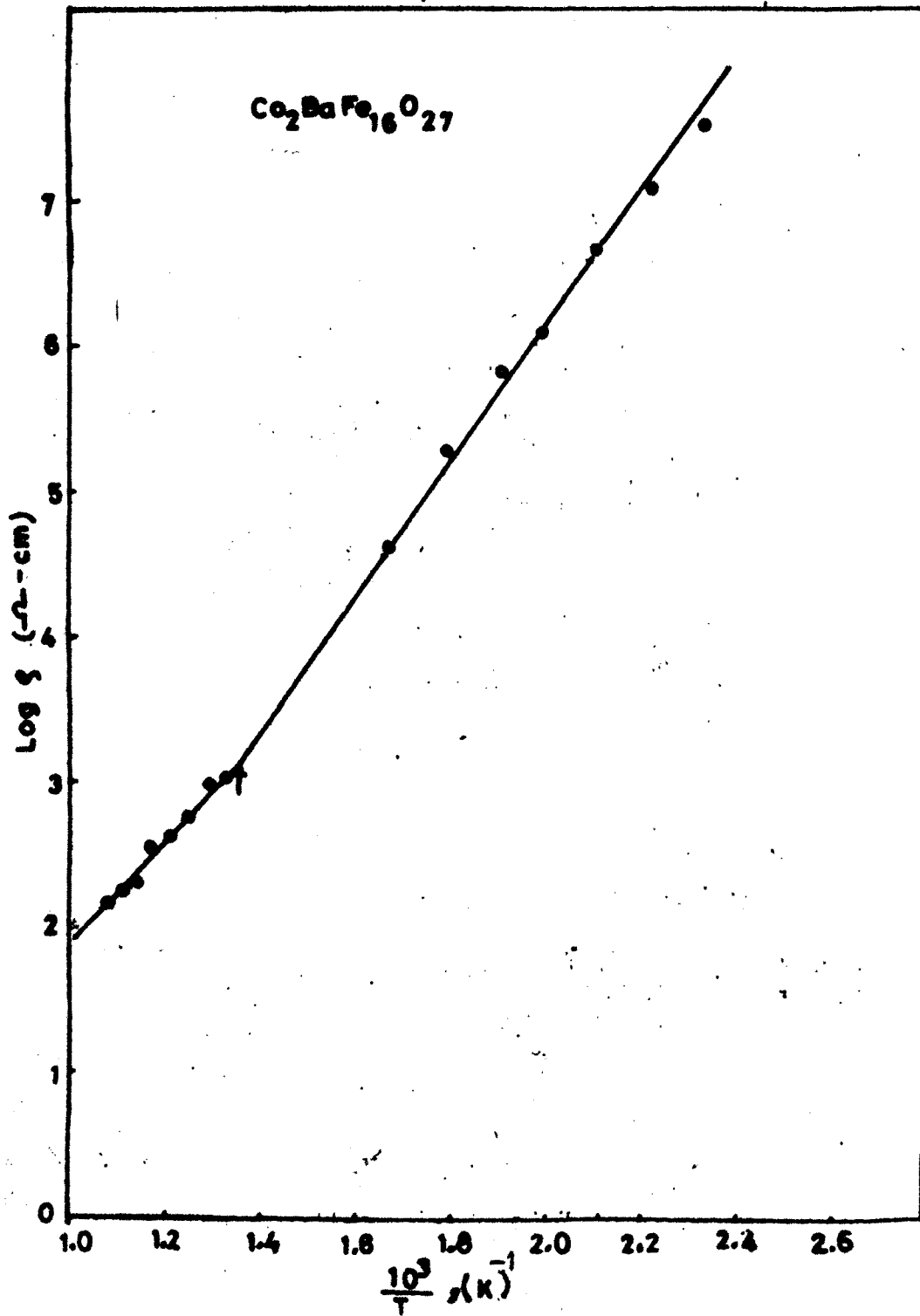


Fig.4.3

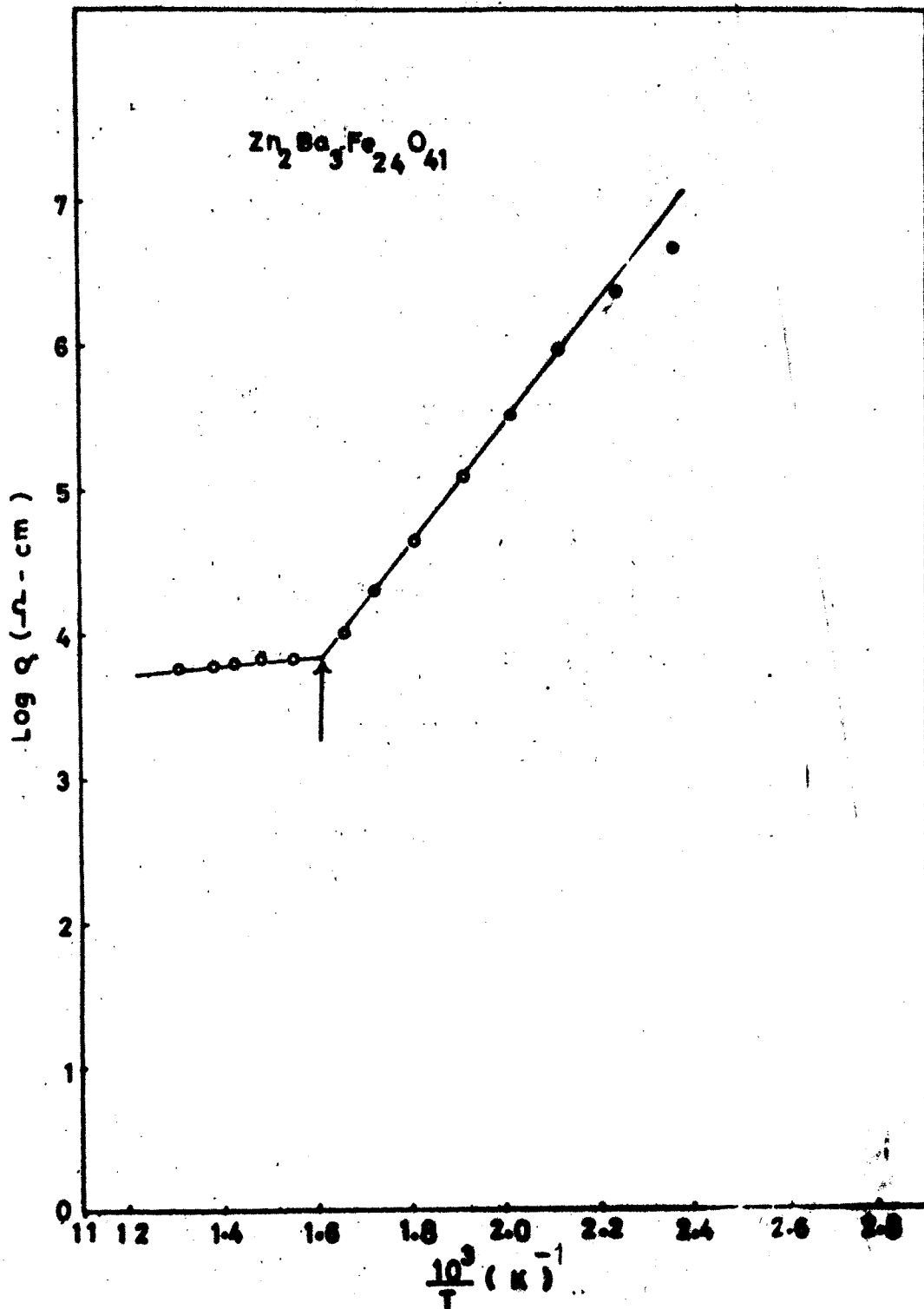


Fig. 44

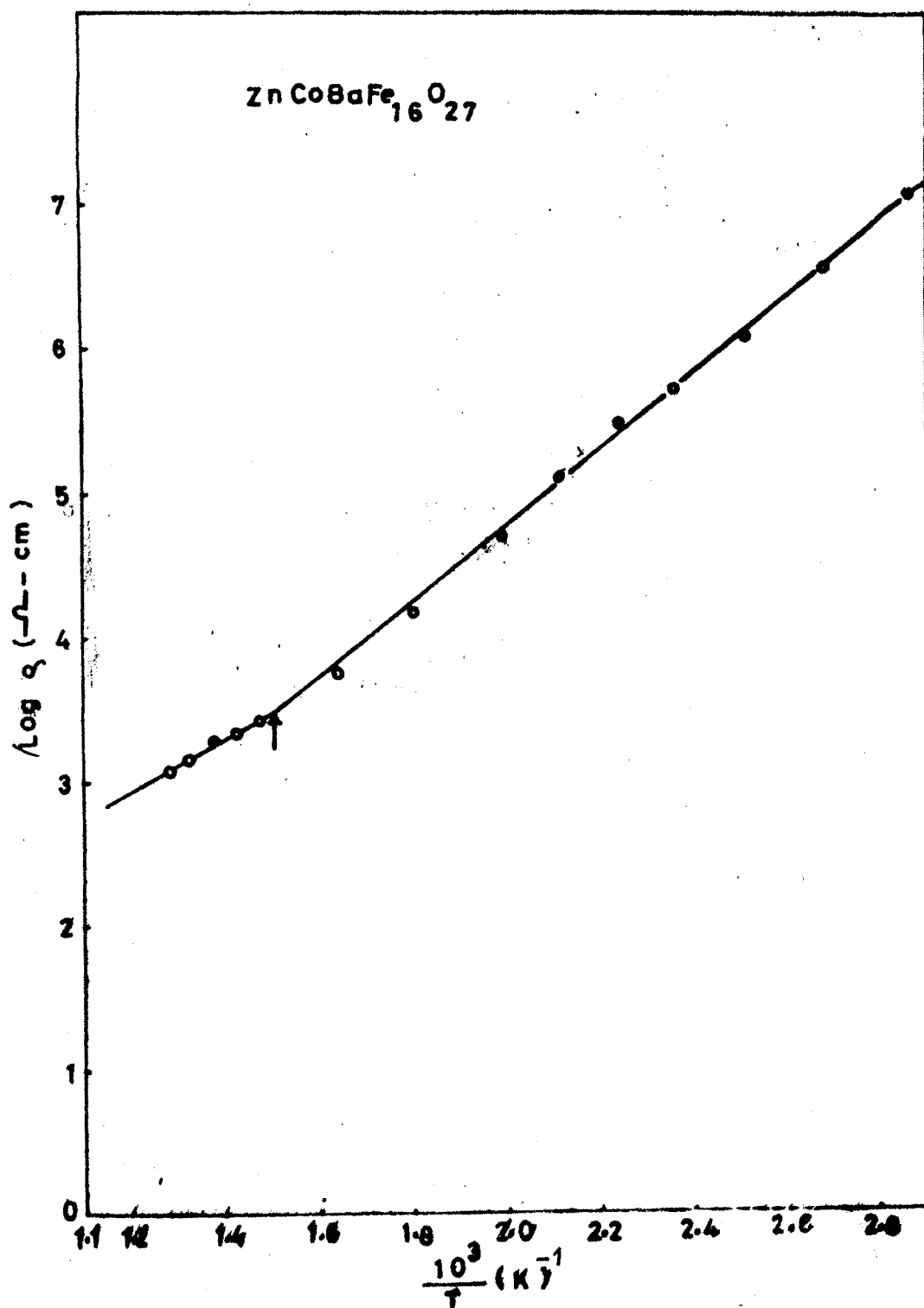


Fig.4.5

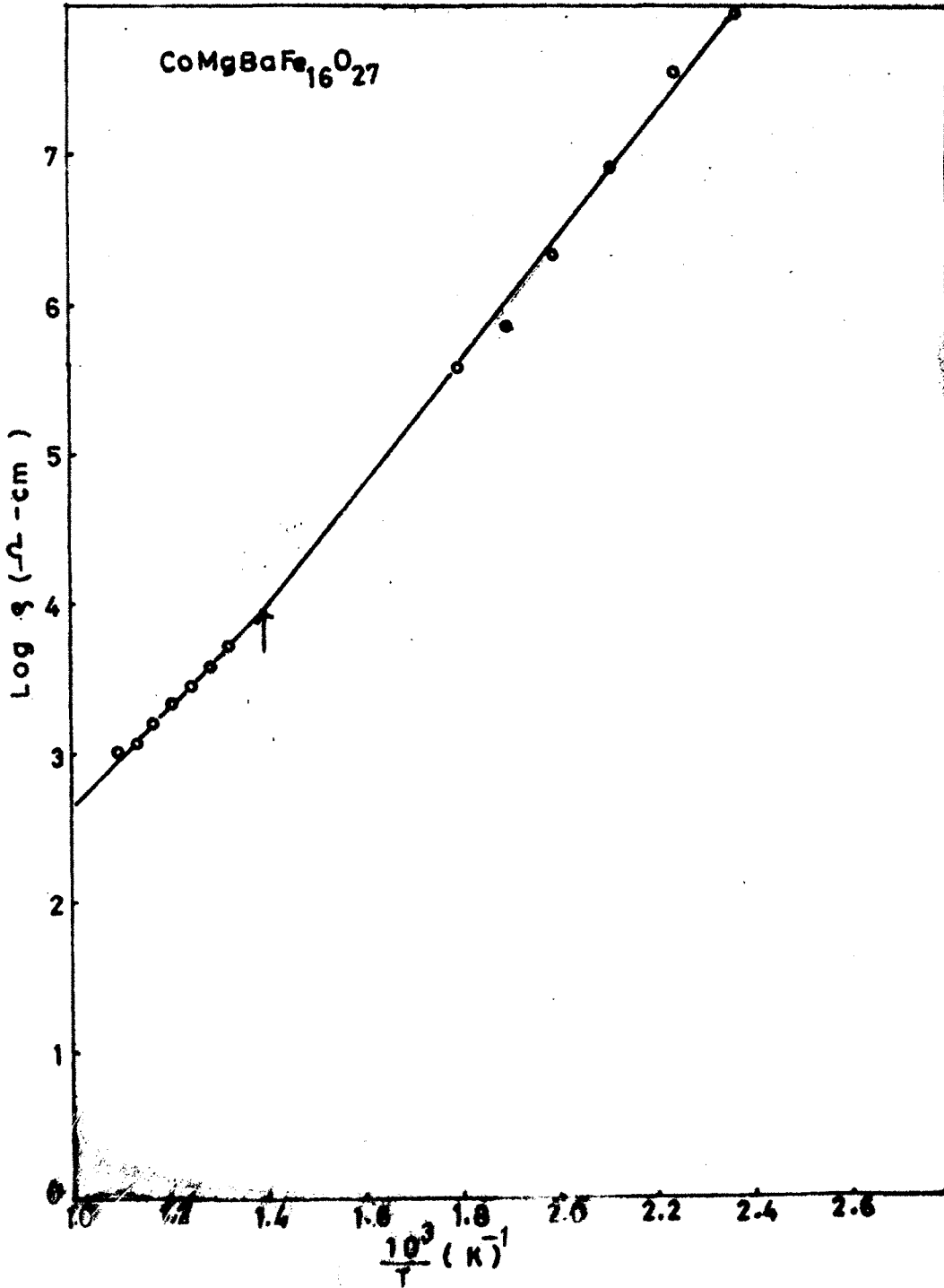


Fig. 4.6

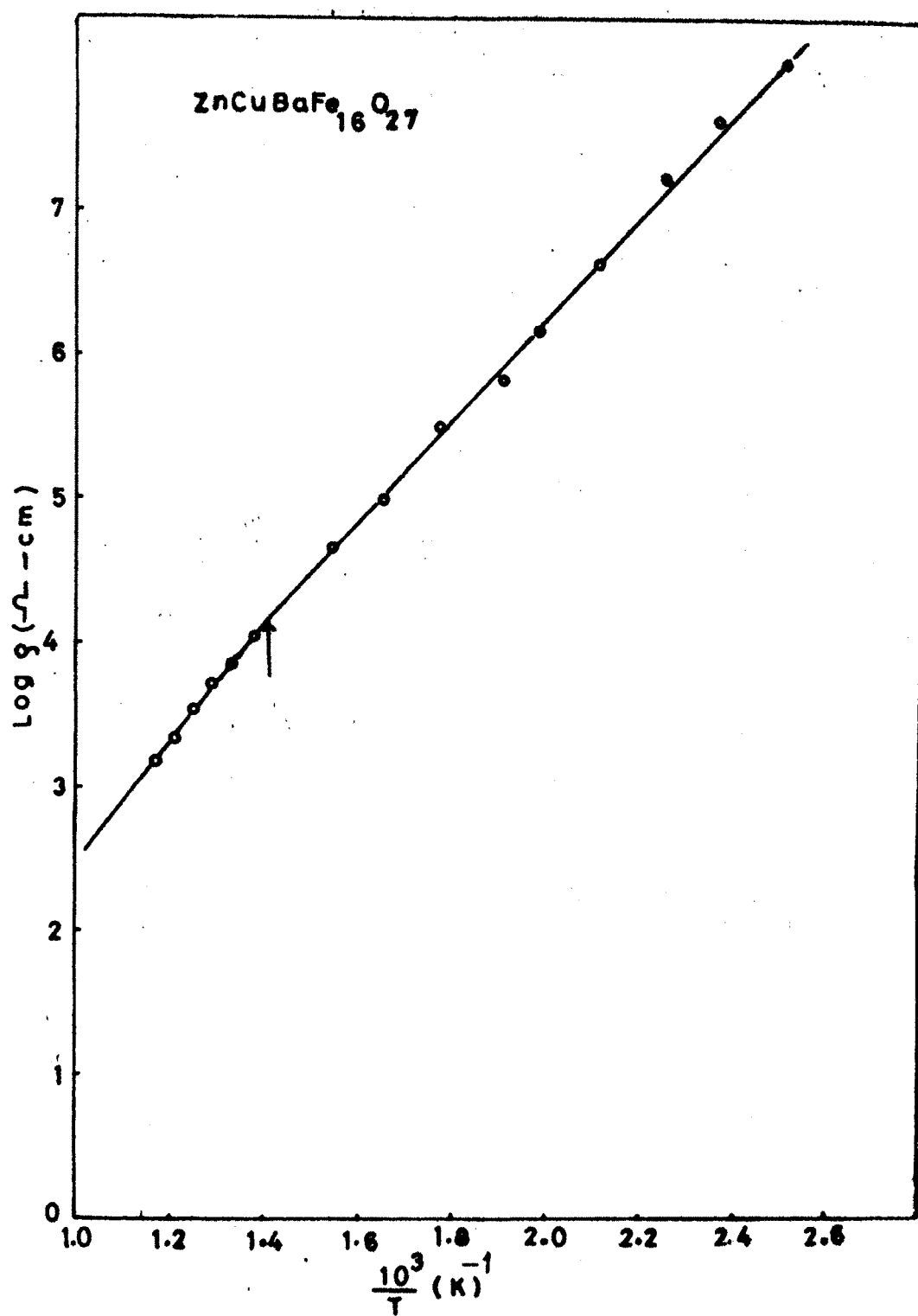


Fig.4.7

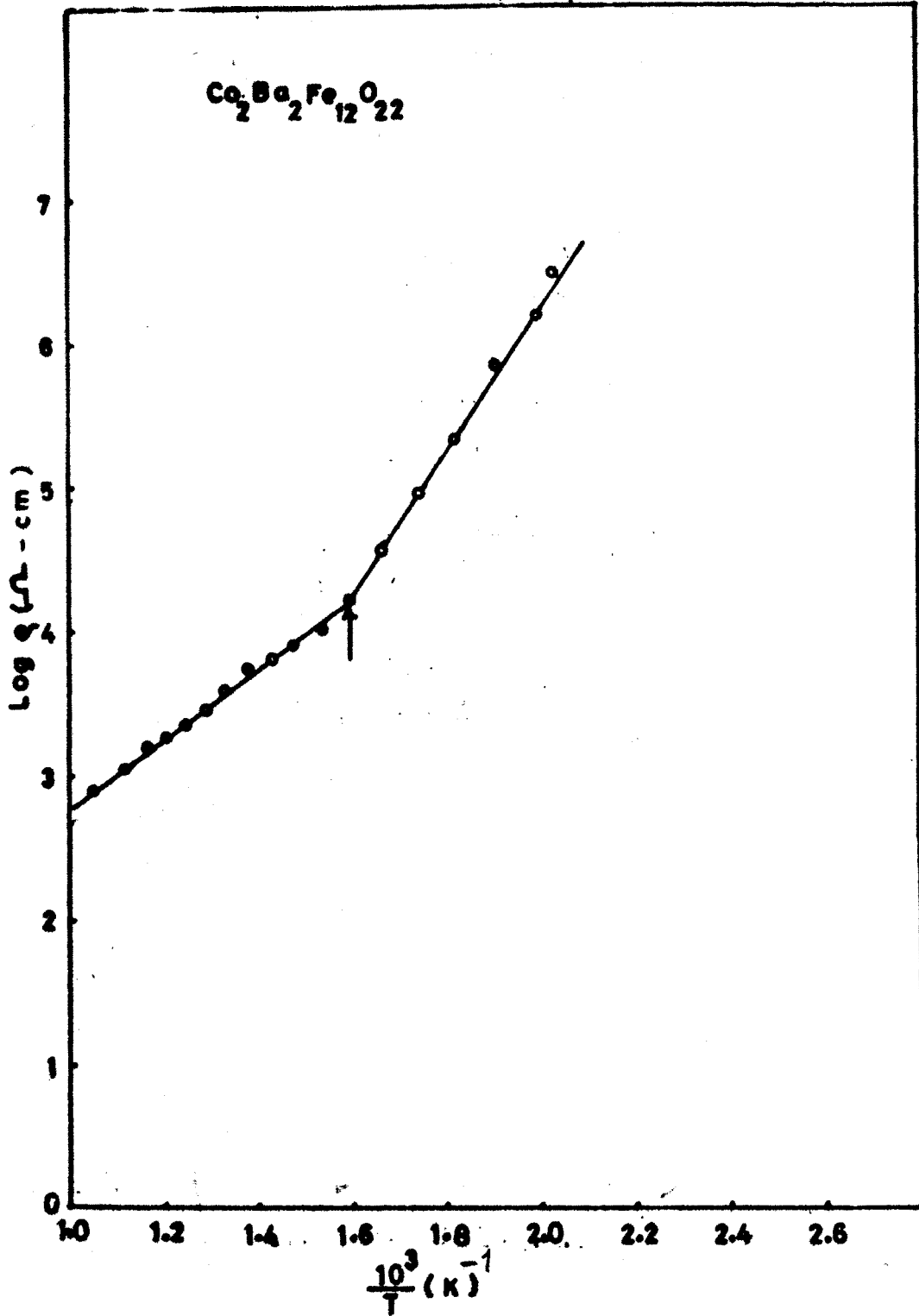


Fig.4.8

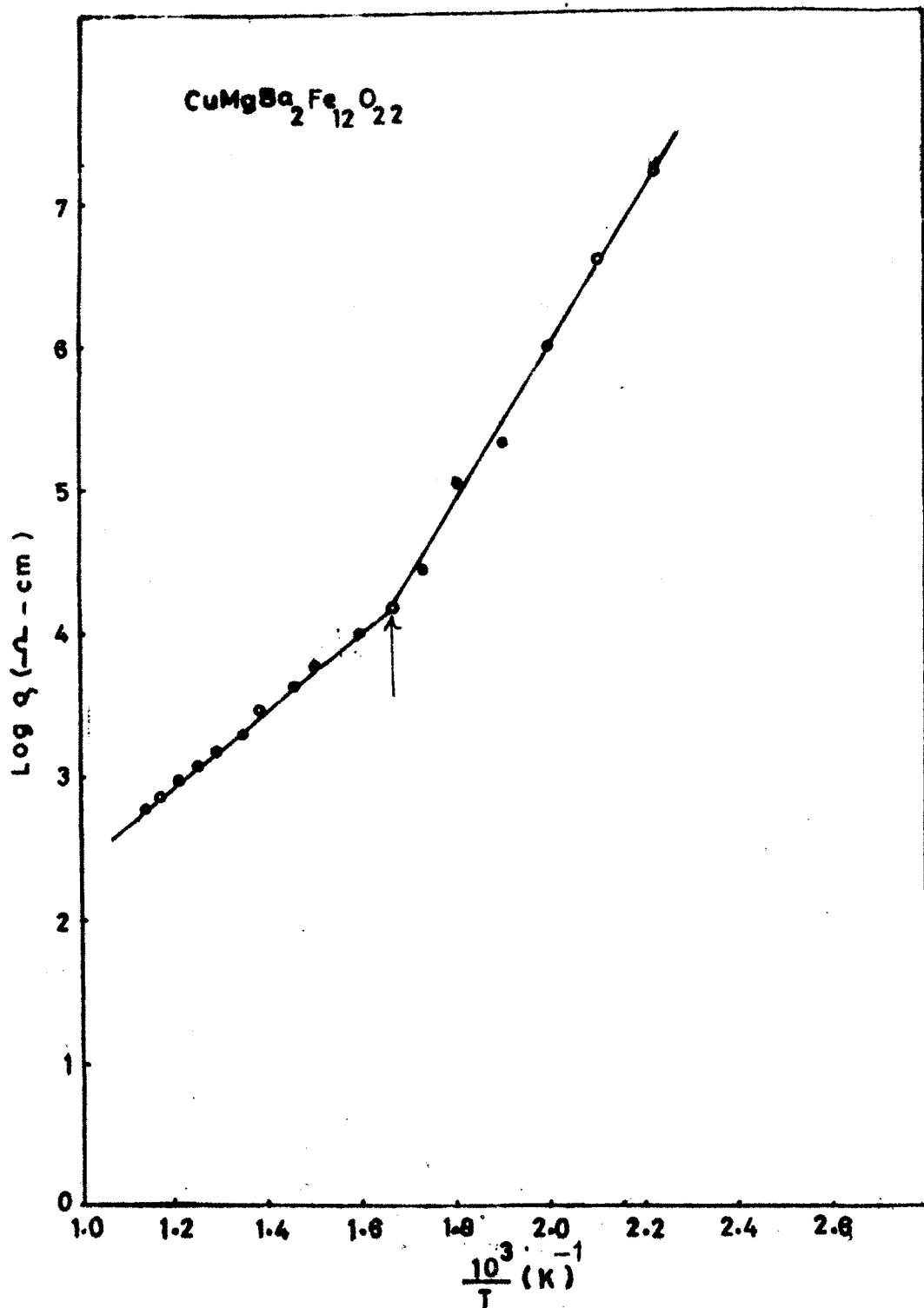


Fig. 4.9

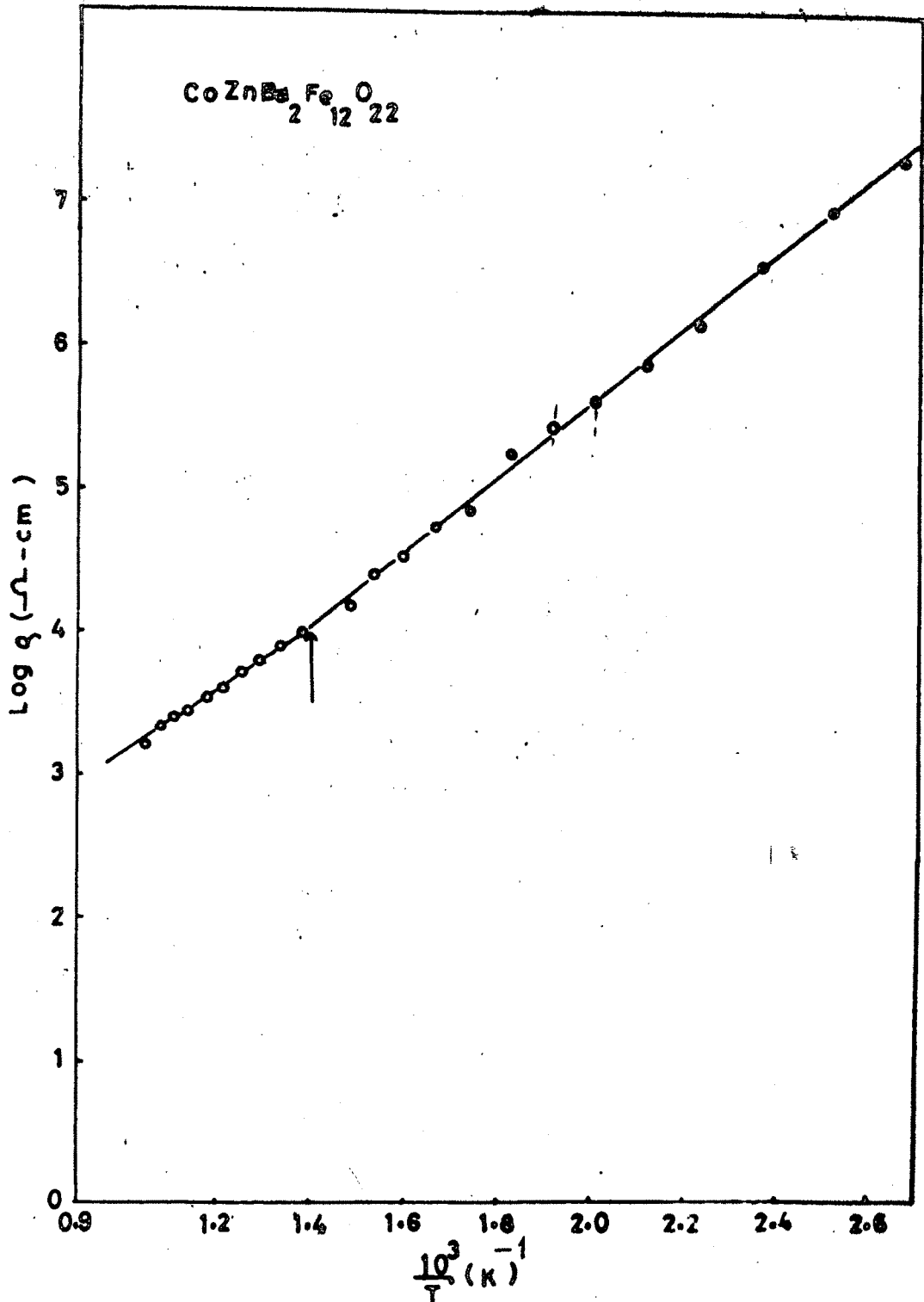


Fig.4.10

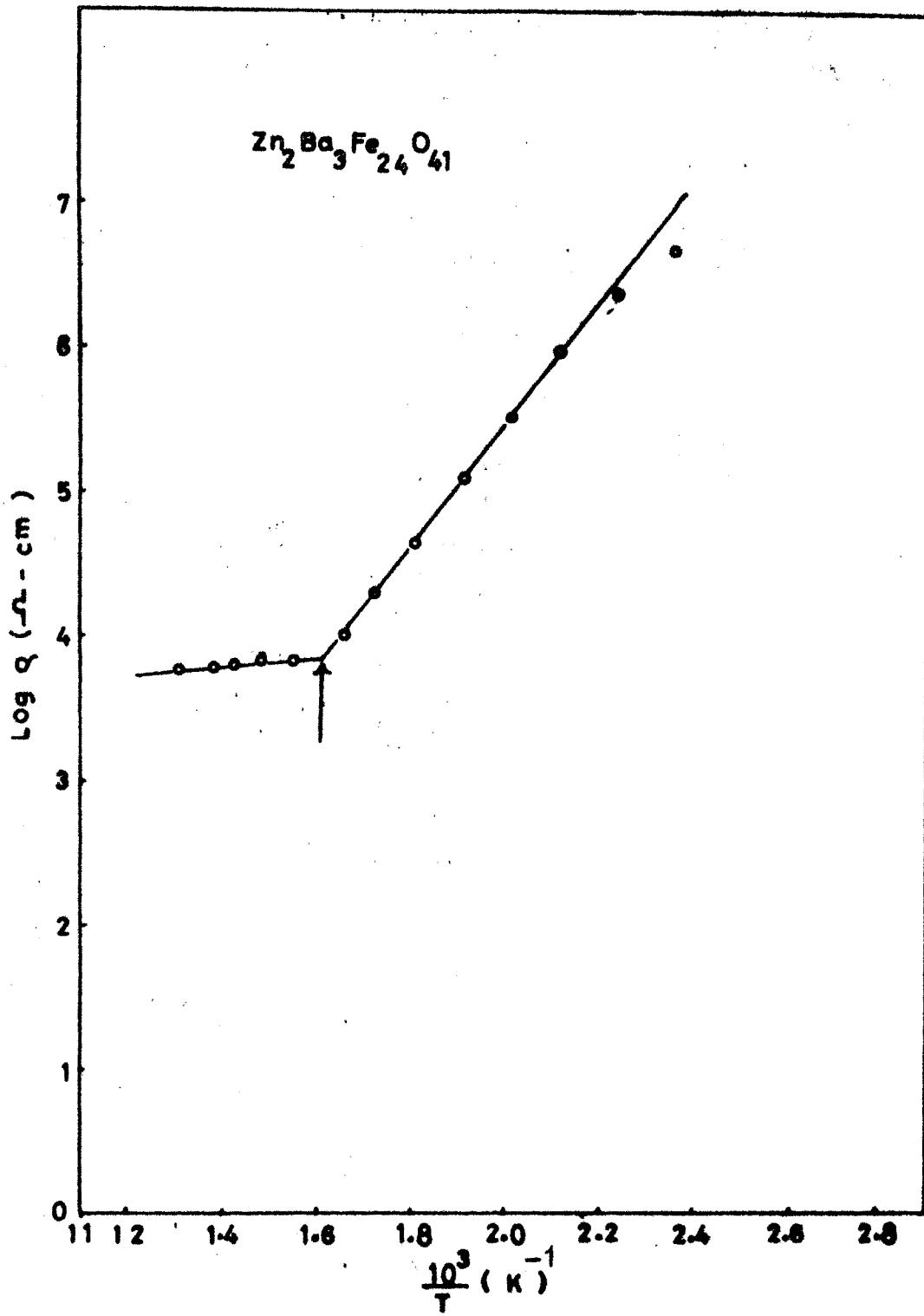


Fig. 4.11

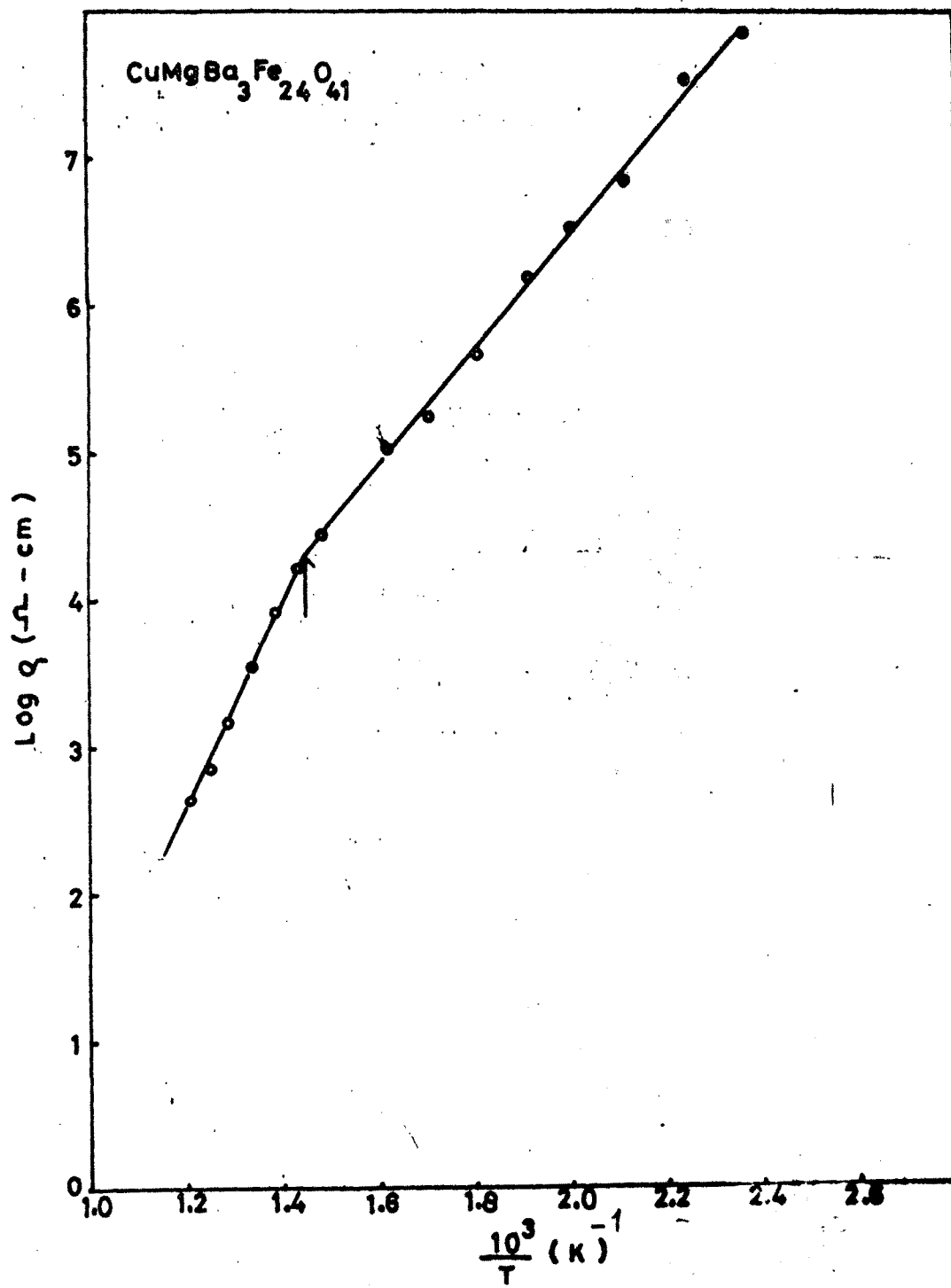


Fig.412

Table 4.1 : Activation + Energies and Curie Temperatures of hexagonal Ferrites.

Sr. No.	Composition	Curie Temperature		Activation energy E (eV)		Inter- action energy KT _c (°K)
		Observed	Other	Ferri	Para	
		T _c ^{°C}	Ref. T _c ^{°C}			
1	BaFe ₁₂ O ₁₉	450	450	0.55	0.15	0.06239
2	SrFe ₁₂ O ₁₉	460	460	0.39	0.41	0.06323
3	Co ₂ BaFe ₁₆ O ₂₇	462	-	0.92	0.71	0.66340
4	Zn ₂ BaFe ₁₆ O ₂₇	416	-	0.50	0.08	0.05943
5	ZnCoBaFe ₁₆ O ₂₇	390	-	0.52	0.35	0.05719
6	CoMgBaFe ₁₆ O ₂₇	441	-	0.81	0.52	0.06158
7	ZnCuBaFe ₁₆ O ₂₇	436	-	0.70	0.82	0.06116
8	Co ₂ Ba ₂ Fe ₁₂ O ₂₂	350	340	0.99	0.56	0.05373
9	CuMgBa ₂ Fe ₁₂ O ₂₂	290	-	0.99	0.53	0.04856
10	CoZnBa ₂ Fe ₁₂ O ₂₂	441	-	0.52	0.44	0.06158
11	Zn ₂ Ba ₃ Fe ₂₄ O ₄₁	348	360	0.84	0.024	0.05356
12	CuMgBa ₃ Fe ₂₄ O ₄₁	416	-	0.77	1.4	0.05943

Fig. 4.1 - 4.12 show that there is a marked change in the the resistivity and hence in the activation energy near the observed curie temperature (Table 4.1). It is an observed fact that the activation energy in the paramagnetic state is generally higher than its counterpart in the ferromagnetic region¹⁴. The lowering of the activation energy has been attributed to the effect of spin ordering on the conduction process in ferrites^{17,18}. A few of the ferrites studied in the present case show such a trend in the change of the activation energy. There are few cases like those of high resistivity, where activation energy changes are very small. Negative results have also been reported for apparently similar materials (e.g. Vernon and Lovell for NiO crystals). The reasons for such discrepancies though not well established, they may be probably thought of to be due to either an accidental onset of defect conduction or some secondary changes like phase transition. The observation of lower activation energy for the conduction process in the paramagnetic region can be attributed to such an effect. (Specimens 1,3-6,8-11, Table 4.1) for the remaining ferrites in our case. In fact such an anomaly has been observed in the case of Cu-Ni ferrites and the same has been recognised to be due to phase transition in these ferrites. These aside quite a fundamental aspects of conductivity features of magnetic oxides remain still un-understood.

The observed curie temperatures agree reasonably well with the previously reported values of curie temperatures by others (Specimens - 1,2,8,11 Table 4.1). Unfortunately no such values could be found for comparison in case of the remaining specimens. Nevertheless, it will be appropriate to note here that the resistivity measurements have been extensively used to determine curie temperatures of ferrite^{13,14,21}_{21 22 23}. Except for the ferrites containing higher amounts of Fe, where curie temperatures differ by amount about 70°C, in all other cases they may well be taken as the representative values.

The additional contribution to resistivity in case ferrites is expected to come from many microstructural changes brought in by the sintering conditions. Polycrystalline ferrites show higher resistivities in the presence of pores. Grain boundaries and other impeding agents (these include even the substituted ions) also play an equally important role. Consequently the activation energies deduced from equation 4 need to be cautiously taken to provide the valuable information on ferrites.

The observed higher values of room temperature resistivities and the activation energies in the present case can be explained with the help of above reasons and the conduction mechanism in ferrites itself. VerWay^{22 (24)} and others have established that in magnetic oxides containing ions of the same parent atom placed in crystallographically similar positions

in the lattice the conduction can take place via activation of the states involving cations of changing valance i.e. $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ and vice-versa. The mechanism, conveniently described as a hopping mechanism, has been successfully used by many workers to explain the electrical properties of many ferrites^{23,24,14}. Electrical measurements made by Zaveta et al.²⁵⁻²⁶ on the single crystals of hexagonal ferrites with 'M' and 'W' structure show a marked anisotropy in the electrical resistivity. From the temperature dependence of resistivity, and from thermoelectric power measurements, it has been established by them that the electron hopping between Fe^{2+} and Fe^{3+} ions plays a prominent role in the conduction process of hexagonal ferrites. The conduction mechanism in the present hexagonal ferrites can also be attributed to such a hopping mechanism. The measurements on thermoelectric power and the chemical analysis are however, necessary to be conducted before coming to such a conclusion. The polarization energy of the ions around the hopping electron, the hopping process some times involves terms like Madelung²⁶ energy, strain energy etc. The peculiarly observed higher activation energies is dictated by these additional energy terms along with the localized nature of the hopping process involving the d wave functions of the current carriers.

R E F E R E N C E S

1. VerWay E.J.W. Haaman P.W., Romejin F.C., Van Oosterhout, G.W.; Phillips Res. Rep. 5 173 (1950)
2. VerWay E.J.W. and de Boer J.H. "Cation arrangement in a few oxides with crystal structure of the spinel type". Recucit des travaux chimiques des pays. Bas. Vol. 55 (1936) P. 531.
3. Van Uitert L.G. Jour. Chemical physics Vol.24 P.306 (1956)
4. De Boer J.H. VerWay E.J.W. Proc. phys. Soc. 49 (extra part) 59 (1937)
5. Craik D.J. (Editor) Magnetic oxides Part 1, P. 421 Wiley Interscience publication (1975)
6. Jonker J.H., J. phys. chem. Solid 9 1965 (1959)
7. Van Uitert L.G., Proc. I.R.E. 44 1294 (1956)
8. Elwell D. Griffiths B.A., Parker R., Brit. J. Appl. phys. 17, 587 (1966)
9. Mott. N.F., Gurney R.W., Electronic processes in Ionic crystals oxford univ. press (1948)
10. Frohlið H.; Adv. phys. 3 325 (1954)
11. Parker R.; Phil. Mag. 3 853 (1958)

12. Parker R. in magnetic oxides (Edi) D.J.Craik
Wiely Interscience publication (1975) P. 442
13. Sawant S.R. and Patil R.N.; Indian J.
Pure and Appl. phys. 20, 353 (1982)
14. Patil S.A., Ph.D. Thesis, Shivaji University
Kolhapur (1980)
15. Anderson, E.E. J.Appl. phys. suppl. 30, 299 (1959)
16. Komar, A.P. and Kliushin V.U.; Bull. Acad.
Sci. USSR 18, 403 (1954)
17. Parker, R., Magnetic oxides Part I Ed. D.J.Craik,
John Wolay and sons (1975) P. 422
18. Rezle Seu, N., Culiurearm, E.,
Phys. stat. sd. (A) 3 873 (1970)
19. Vernon, M.W. and Lovell, M.C.
J. phys. chem. sol. 27, 1125 (1966)
20. Ghami, A.A.: Eatal, A.I. and Mohmed A.A.,;
proc. Int. conf. on Ferrites; 216
(Sept.-Oct. 1980) Japan.
21. Komar A.P. and Klivshin, Bull Y.V.
Acad. Sci. USSR phys. sev.(USA) 18 96 (1954)
22. VerWay, E.J.W. and de Boer J.H.
Recucit des travaux chimiques des.
phys. Bas. vol. 55, p. 531 (1936)

23. Rezlescu N., Rezlescu, E. Sol. Stat. commun
14 69 (1974)
24. Sisma, Z., Simsova, J; Borabera V.A.M.,
Proc. 11th Int. conf. on Prog. of
Semiconductors, Warsaw, Poland. 2 1294 (1972)
25. Zaveta, K. phys. stat. Sol. 3, 2111 (1963)
26. Zaveta K. Sisma Z. and Zalesskij A.V.
phys. stat. Sol. 14 485 (1966)