

*Chapter - IV***DC ELECTRICAL RESISTIVITY**

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4.0 Introduction

The electrical properties of ferrites are affected by the amount of divalent iron ion, the distribution of cations, non-magnetic and magnetic substitution of cations in the sites, sintering conditions, grain size and grain growth [1]. Verwey and deBoer [2] explained the conductivity of ferrites on the basis of hopping mechanism. Klinger [3] has explained the conduction mechanism in magnetite using two phase polaron model. He concluded that at high temperature, the conductivity is due to weakly activated tunneling motion of polarons and at low temperature, it is due to strongly activated motion of correlated polarons.

There are various contributions to the inherent resistivity of the solid ferrites, which are [4]

1. Sintered polycrystalline sample contain air filled pores, which affect the actual resistivity of ferrites.
2. The grain size, number of grains or grain contacts in a polycrystalline sample influences the conduction path and hence the resistivity.
3. The chemical and heat treatment may result in chemical inhomogeneity.

The effect of iron stoichiometry and sintering temperature on resistivity of nickel ferrite has been investigated by Van - Uiteret [5]. The dependence of resistivity and activation energy of nickel zinc ferrites on sintering

temperature and porosity is studied by Naik and Powar [6]. They observed that, the resistivity, porosity and activation energy considerably reduces at higher sintering temperature. Economos [7] showed that the preparation of ferrite under different firing atmosphere affects the resistivity. Koops [8] studied the electrical conductivity of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ fired under different conditions and found that the conductivity depends on the preparation technique. R.K. Puri et al [9] studied the electrical and magnetic properties of normal and hot pressed nickel substituted Mn-Zn ferrites of different compositions. They observed that resistivity of normal ferrites is greater than that of hot pressed ferrites. He attributed it to low intergranular porosity. Bhise et al [10] have shown that the resistivity of Ni-Zn ferrites increases with increasing concentration on Mn^{2+} , Ti^{4+} ions.

The electrical resistivity of tin substituted nickel ferrite as a function of composition and temperature is studied by Bajjal et al [11]. They observed that the resistivity of nickel ferrites increases with increasing tin content.

Ahamand et al [12] have reported the resistivity and thermoelectrical power of Ni-Al ferrites. They found that the resistivity and activation energy increases with addition of aluminum. Suckov [13] and Ifte et al [14] investigated the electrical properties of iron deficient Ni-Zn ferrites.

The electrical properties of nickel and nickel-zinc ferrites have been studied by several investigators [15-19].

4.1 Conduction in oxides

Similar to other semiconducting oxides, the resistivity of ferrite is affected by the presence of impurities. The electronic conduction in oxides is associated with the presence of ions of a given element in more than one valance state distributed randomly over crystallographically equivalent lattice sites [2]. The conduction in high resistivity oxides can be enhanced by incorporating very small amounts of foreign oxides into the structure whose metal ions takes valancies other than that of the host [20].

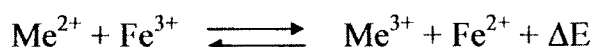
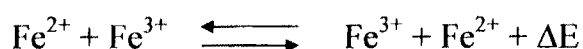
The activation energy plays a major role in the conduction mechanism of oxides. It depends on the difference between ionization energy and electron affinity of the free divalent ions, the difference in energy of the two configurations, the difference in stabilization of crystal field above configuration and the polarization energy of the surrounding crystal lattice.

4.2 Conduction in ferrites

At room temperature resistivity of ferrite vary from $5 \times 10^{-3} \Omega\text{cm}$ in case of magnetite [21] to well over $10^{11} \Omega\text{cm}$ in case of certain magnesium and nickel ferrites [22]. These low and high resistivities of ferrites are explained on the basis of actual location of cation in the spinal structure and the hopping mechanism. The low resistivity of ferrite is due to the simultaneous presence of ferrous and ferric ions in the crystallographically equivalent sites [2]. The high resistivity in ferrites is associated with the occupation of divalent metal

ions and trivalent iron ions on octahedral sites [36]. Such an arrangement requires higher activation energy for hopping of electrons.

The two mechanisms of conductivity can be represented as



where Me- represents the divalent metal ion like Co, Ni, Mg, Mn etc. and ΔE is the activation energy required to transfer the electron from Me^{2+} to Fe^{3+} and vice versa.

The conduction mechanism in ferrites is described either by using the band picture or hopping model. According to band model the temperature dependence of conductivity is mainly due to the variation of charge carrier concentration with temperature, while in the hopping model the change of their mobility with temperature is considered to constitute current by jumping or hopping of electrons from one iron ion to the next.

The conductivity of ferrites cannot be explained on the basis of the free electrons model, because of the fact that the electrons in ferrites are not free and energy band model fails to explain the electrical properties for the lack of the Bloch type wave functions in ferrites [1]. However, conductivity of ferrite can be explained in terms of electronic charge carriers like electrons and holes by the usual relation.

$$\sigma = e (n_e \mu_e + n_h \mu_h)$$

.... 4.1

where n_e and μ_h stands for concentration of electrons and holes. n_e and μ_h stands for mobilities of electrons and holes respectively.

The hopping mechanism of conductivity in ferrites is associated with activation energy, which can be calculated from $\log \rho$ versus $1/T$ plots. As temperature increases, the ferrite changes its magnetic state from a ordered ferrimagnetic state to a disordered paramagnetic state. When such a change occurs there is an abrupt change in activation energy. Activation energy in ferrimagnetic region is less than the activation energy in paramagnetic region.

In ferrites, two types of scattering exists one is the lattice scattering and other is impurity scattering. The lattice scattering increases with increasing amplitude of variation at higher temperature. The mobility is proportional to mean free path between scattering events. Hence conductivity becomes temperature dependent and is written as

$$\sigma = \sigma_0 \exp (-\Delta E/KT) \quad \dots 4.2$$

where σ_0 - temperature dependent constant

K - Boltzmann constant

In ferrite lattice there is an interaction between the orbitals of neighbouring ions and electrons, resulting into the polarization of the lattice. This effect is more pronounced due to strong coulomb interaction in ionic crystals such as ferrites. The combination of electron and polarization field is called as polaron. When such association is weak, it constitutes large polarons. Such a polarons are found in ionic crystals. But when the electron

plus lattice deformation has a linear dimension smaller than lattice constant, it constitutes smaller polarons. Usually they are found in covalent crystals. Due to such deformation, the effective mass of electron increases as it partially drags the ion along with it. Therefore the mobility of electron decreases and becomes highly temperature dependent.

With the help of binding energy E_p of the electron and the polarized lattice, the mobility of the electron can be written as,

$$\mu_{\text{polaron}} \propto \exp(-E_p/KT) \quad \dots 4.3$$

where $E_p = e^2 / K_{\text{eff}} \cdot v_p$

where v_p - dimension of lattice deformation, $1/k_{\text{eff}}$ - the difference of reciprocal of the optical and static dielectric constant.

With the help of the small polarons, the conductivity is related to E_p , E_g and T by the relation

$$\sigma \propto n\mu_{\alpha} \exp [(-E_g/KT) - (E_p-KT)] \quad \dots 4.4$$

Due to polarization the electrons are trapped at the potential well. When such a potential well is deep enough, the electrons may be trapped at lattice site. Therefore its transition to neighbouring site may be determined by the thermal activation. Hence due to thermal activation, lattice is set into periodic vibrations which are quantized into phonons.

At high temperature electrons jump from one site to another by thermal activation. The hopping mechanism contributes to conductivity at high

temperature. At low temperature electrons tunnel slowly through the crystal resulting into small conductivity.

The temperature dependent mobility [23] is given by

$$\mu = \frac{e^2 a^2 \omega^2}{KT} \exp(\Delta E/KT) \quad \dots 4.5$$

where ω - polaron frequency and a - jump length

At low temperatures, polarons behave as particles moving in narrow band, whereas at high temperature small polaron motion results by the absorption of one or more phonons. Therefore the process is essentially a hopping mechanism. When a tunneling time is less than the time for successive hopping transition, conduction by small polarons becomes more predominant. The small polaron model for conductivity mechanism is explained earlier [24-28].

4.3 Experimental

The dc resistivity measurement of the system $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ (where $x=0; 0.20; 0.40; 0.60; 0.80$ and 1.00) was carried out by using two probe method. The conductivity cell and electrical circuit for resistivity measurement are shown in Figure 4.1.

The experimental setup consists of furnace, power supply unit, an adapter and a digital dc microvoltmeter. To obtain good ohmic contact, the sintered pellet was sandwiched between two silver electrodes and held tightly between the copper rods with the help of screws. The sample holder was then

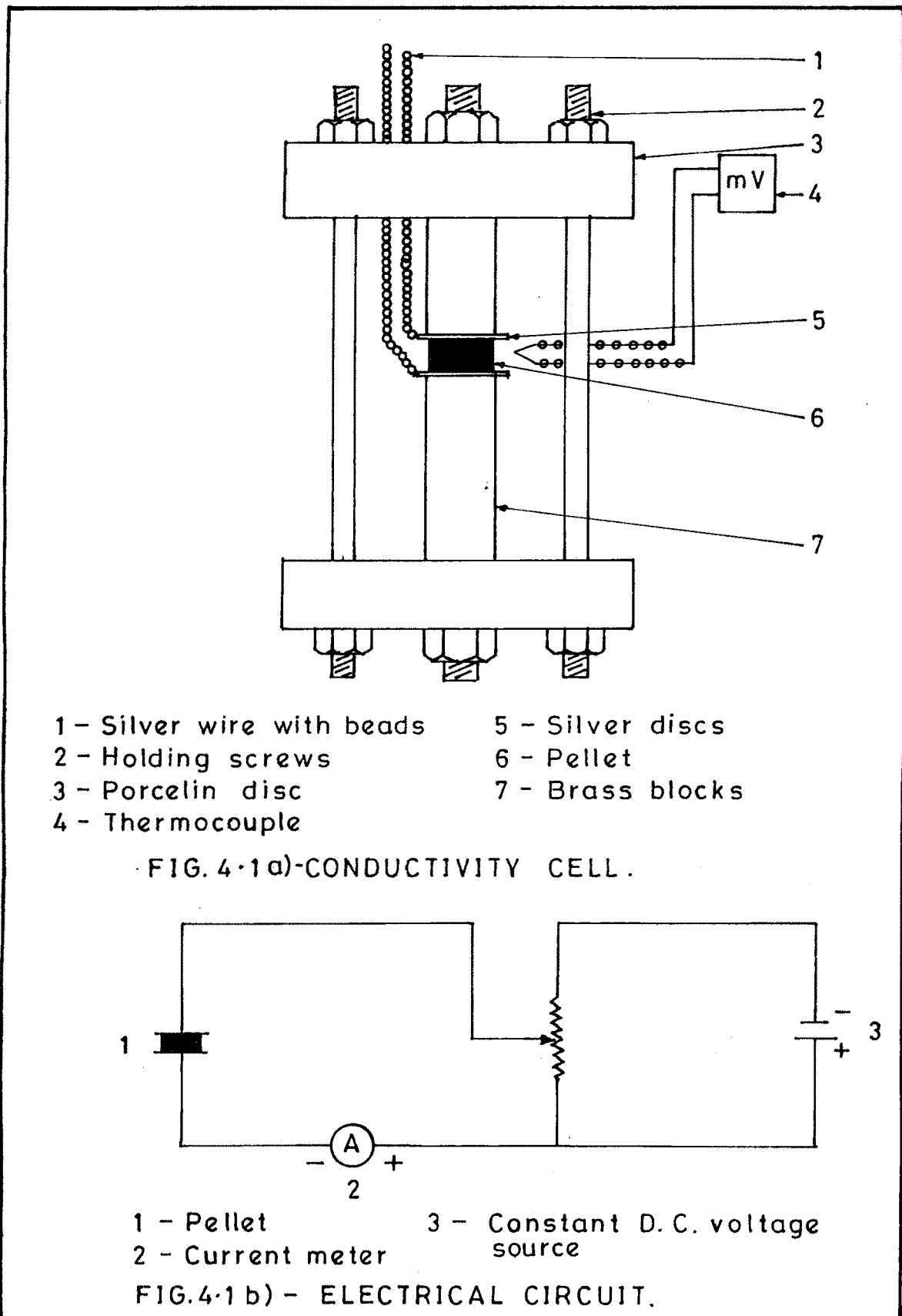


FIG. 4-1- (a) CONDUCTIVITY CELL.
 (b) ELECTRICAL CIRCUIT FOR RESISTIVITY MEASUREMENT.

placed in the furnace. A calibrated cromel- alumel thermocouple was used to measure the temperature of furnace. The current (I) flowing in the circuit was measured at a constant voltage of 3 Volts (v) from room temperature to 850 K. The resistivity was calculated by using the relation.

$$\rho = \frac{\pi^2 r^2 V}{t I} \quad \dots 4.6$$

where t - thickness of pellet and r - radius of pellet

4.4 Results and discussion

The plots of $\log \rho$ versus $10^4/T$ for the $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ sample with compositions $x = 0, 0.20, 0.40, 0.60, 0.80$ and 1.00 are presented in figure 4.2. The figure, shows that the resistivity decreases with increasing temperature obeying Arrhenius relation,

$$\rho = \rho_0 \exp (\Delta E/KT) \quad \dots 4.7$$

where ΔE - activation energy

K - Boltzmann constant

ρ_0 - temperature independent factor.

Further it shows that there are two distinct regions for compositions $x \leq 0.80$ separated at magnetic transformation temperature called as Curie temperature (T_c).

Irkhin and Turov [29] have shown that the change in the slope of the straight line should occur while passing through the Curie point. The Curie

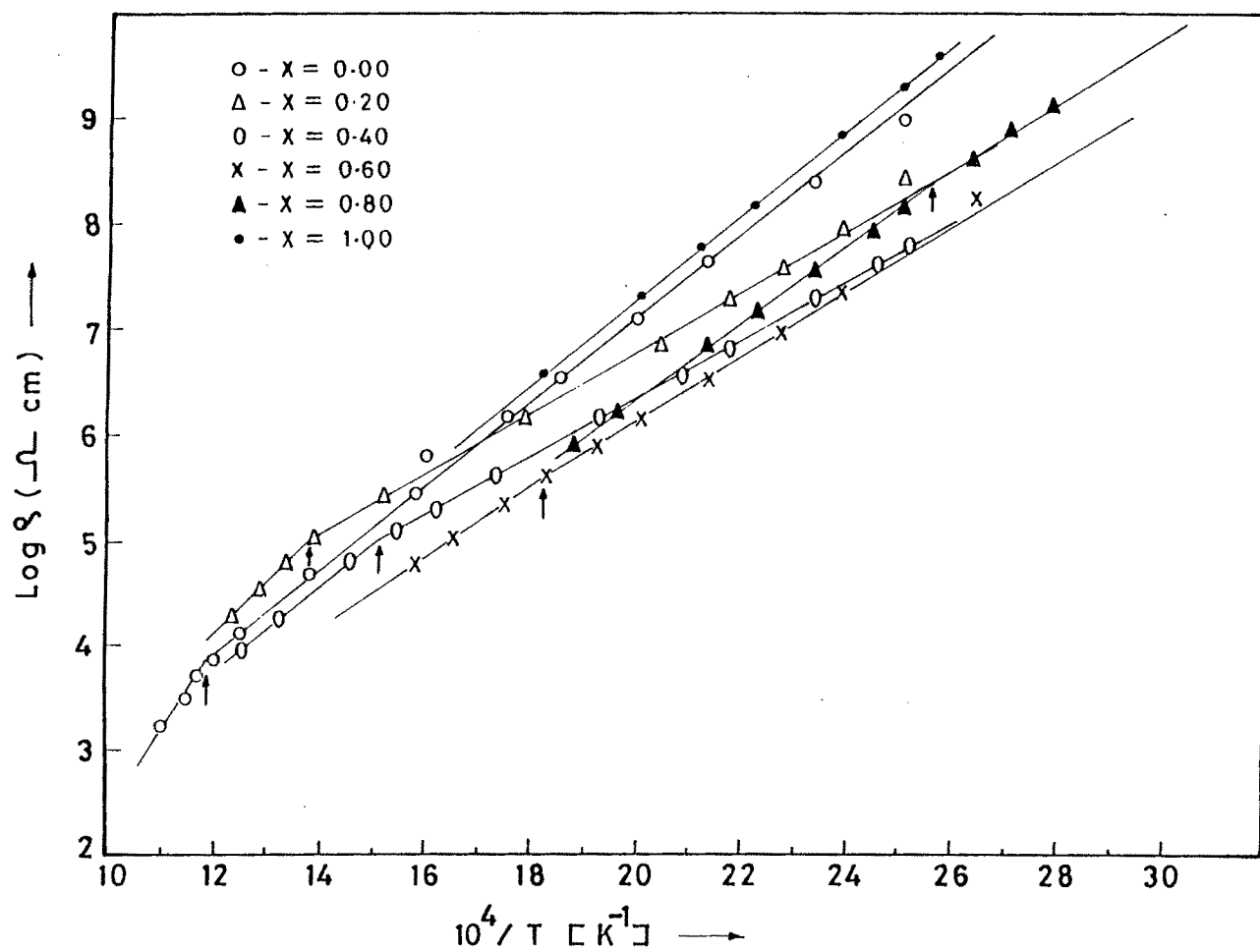


FIG. 4-2 - VARIATION OF LOG ρ VERSUS $10^4/T$ FOR $Ni_{1-x}Zn_xFe_2O_4$ SYSTEM.

point separates the upper ferrimagnetic region from the lower paramagnetic region, as the spin-spin interaction vanishes due to thermal vibrations. Similar result is reported by Komar and Kilvshin [30] in the case of several ferrites.

Ghani et al [31] have observed three regions in temperature variation of resistivity for Cu-Ni ferrites. According to them, the first region is due to the presence of impurities, the second region is due to phase transition and third is due to magnetic ordering change. Similar behaviour is observed in case of Mn substituted Ni-Zn ferrites by Bhise et al [32]. Electrical conductivity of copper substituted and non-substituted Ni-Zn ferrites is studied by Joshi et al [33]. They observed four different regions in the resistivity versus temperature plots for Ni-Zn ferrites.

The composition $x= 1.00$ exhibits paramagnetic behavior at and above room temperature.

From figure 4.2. it can also be noticed that the resistivity of zinc ferrite is higher than that of nickel ferrite and zinc substituted nickel ferrites. The resistivity of nickel ferrite at Curie temperature was observed to be $3.2 \times 10^4 \Omega\text{cm}$, while Parker [34], Reddy and Rao [35] have reported it to be about $10^4 \Omega\text{cm}$. Van Uitert has studied the resistivity of polycrystalline Ni-Zn ferrite of various compositions and has shown that, the composition $\text{Zn}_{0.3}\text{Ni}_{0.7}\text{Fe}_2\text{O}_4$ has minimum conductivity. He attributed it to the electron-hole compensation [36]. In zinc substituted nickel ferrites ($x=0.20, 0.40, 0.60$ & 0.80), we [37], observed the maximum resistivity for $x=0.20$. For further

addition of Zinc, resistivity decreases upto $x=0.60$ composition and then increases for $x=0.80$. For lower concentration of Zinc, the conduction is due to hole transfer from Ni^{3+} to Ni^{2+} ions [2].



whereas in case of higher concentration of zinc, the conduction is due to the hopping of electrons from Fe^{2+} to Fe^{3+} ions [5].

The activation energies corresponding to the paramagnetic and ferrimagnetic regions are calculated by using equation 4.7 and Fig. 4.1 and presented in Table 4.1. along with resistivity data at about $500^{\circ}C$. The activation energy in paramagnetic region is found to be higher than that of ferrimagnetic region which is in agreement with the reported results by Satyanarayana and Murthy [18]. The reduction in resistivity is just consequence of reduction in activation energy [6].

Table 4.1

Resistivity, activation energy and curie temperature data of

$Ni_{1-x}Zn_xFe_2O_4$ system

Zinc content x	Resistivity at 500 K $\Omega cm 10^6$	Activation energy eV		Curie temp. (T_c) $^{\circ}C$
		Para region	Ferri region	
0	5.385	1.190	0.934	574
0.20	5.560	1.172	0.551	478
0.40	1.967	0.882	0.472	376
0.60	1.484	0.551	0.331	276
0.80	2.052	0.760	0.632	119
1.0	20.104	0.793	-	-

We [37] observed that the resistivity of ferrite prepared by oxalate precipitation method is higher than the reported values of resistivity of ferrite prepared by ceramic method [6]. The reduction in resistivity of ferrite prepared by ceramic method is explained in terms of an increase in Fe^{2+} concentration caused by the evaporation of zinc during sintering [1, 38, 39].

Recently, Verma et al [40] have prepared high resistivity nickel -zinc ferrites by the citrate precursors method. They observed that resistivity of Ni-Zn ferrites prepared by this method has higher resistivity than that reported for ferrites prepared by conventional ceramic method. They attributed it to the reduction in Fe^{2+} content of the ferrites.

At room temperature, the resistivity of $\text{Ni}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$ in the present method is $1.15 \times 10^9 \Omega\text{cm}$. However, reported value of resistivity of the same composition prepared by citrate method is $1.5 \times 10^8 \Omega\text{cm}$ [40].

The values of transition temperatures (T_c) observed from $\log\rho$ versus $10^4/T$ plots are presented in table 4.1. From this table, it is clear that the transition temperature decreases with increasing zinc content. Such a variation can be explained on the basis of strength of A-B interaction. As the content of Zn^{2+} ions increases in the sample, the number of Fe^{3+} ions on A site go on decreasing, which results decrease in A-B interaction and hence the Curie temperature decreases.

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