Polaronic Relaxation and Variable-Range-Hopping Conductivity in Fe$_3$O$_4$ Nanoparticles

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Abstract. We report the polaronic relaxation and Variable Range Hopping (VRH) conductivity in 100nm average particle size cold pressed Fe$_3$O$_4$ nanoparticles. The crystal structure was studied using XRD showing spinel structure with (311) intense peak. The AC transport in the cold pressed powder was studied from 10 K to room temperature and from 100 Hz to 5.5 MHz. It was observed that the solid couples capacitively with the perturbing electric field initially and as the frequency increases it becomes more inductive. The impedance data was modelled using modified Havriliak–Negami relaxation model. It was observed that the cold pressing introduces an asymmetric broadening in the relaxation process. The change in impedance with temperature showed a drastic drop at around 120 K due to Verwey transition in real as well as imaginary part. The change in DC resistance with temperature indicated VRH mechanism of charge transport in the solid with a metal insulator transition at around 120 K. The relaxation times calculated indicated that the hopping process has an attempt frequency of the order of 30 microseconds. The activation energy change across the phase transition with relaxation time and resistance indicated that the charge transport is coherent. The activation energy of ~0.05eV above Varway transition indicated that the transport is small polaronic in nature.

1. Introduction

Half metallic solids are extensively studied for many years since these are an ideal component for spintronic devices. These show spin dependent scattering and strong electron-electron correlation, resulting in metal insulator phase transition [1]. Bulk Fe$_3$O$_4$ exhibits half metallicity with theoretically 100% spin polarization [2]. The dynamic magnetic and semiconducting properties provide a prominent role to Fe$_3$O$_4$ in the development of oxide electronics [3]. Fe$_3$O$_4$ has mixed iron valences of Fe$^{3+}$ and Fe$^{2+}$. It shows inverse-spinel cubic structure(AB$_2$O$_4$) at ambient conditions. Upon cooling below a certain temperature it shows exceptional discontinuous drop in the electrical conductivity termed as Verwey Transition (T$_V$). The metallic nature at T$>$ T$_V$ could be explained by the charge disorder (CD) within the B sites as well as the metal-insulator transition below T$_V$ is due to the charge ordering (CO) [4]. The electrical transport in Fe$_3$O$_4$ is drastically affected by the dimensionality of the solid. At lower dimensions the T$_V$ as well as the electrical resistance gets affected by the particle size in nanoparticles [5] as well as thickness of the films [6]. The measurement of electrical transport at lower dimensions preserving the dimensionality is a challenge. The heat treatment to the powder or film for compacting changes the very governing parameters like particle size or grain size leading to loss of dimensionality effect [7].

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In the present work we investigate the charge transport properties of Fe$_3$O$_4$ nanoparticles in cold pressed condition preserving the effect of the dimensionality [8], which is difficult to achieve if the particles are thermally treated. The Fe$_3$O$_4$ powder of average 100nm size is subjected to dielectric relaxation study from 10 K to room temperature. The relaxation was modelled using asymmetric-dissipative Havriliak–Negami (HN) dispersion model [9]. The relaxation time and the asymmetry parameters are studied to interpret the effect of charge ordering across T$_c$ with variation of frequency.

2. Experimental

The 99 % pure Fe$_3$O$_4$ nanoparticles having average size 100 nm were commercially purchased from Sigma Aldrich. The crystal structure of the same was studied by the PROTO AXRD Powder diffractometer. The patterns with Cu Kα radiation ($\lambda=1.5405$ Å) were recorded in the region 20$^\circ$ to 80$^\circ$. The powder was cold pressed and compacted for 30 minutes under pressure. The pellet formed was coated with silver to form electrodes. The low temperature electrical measurements were done in Advanced Research Systems, Inc. CCR (Closed Cryogenic Refrigerator), along with lakeshore temperature controller model 335. To analyse the impedance response, ZM2376 LCR meter of frequency range from 1mHz to 5.5 MHz was used. Parameters like R$_p$, X, C$_p$, D were measured on various temperatures from room temperature to 10 K. To avoid electrode effects the measurements are accounted only from 100 Hz to 5.5 MHz.

3. Results and Discussion

Figure 1 shows the XRD pattern of Fe$_3$O$_4$ nanoparticles with high intense peaks at (311) crystal plane with no characteristic peaks of impurities (indexed with JCPDS 19-0629) which infers the inverse cubic spinel structure. The particle size was found using the Debye-Scherer formula $d = K\lambda/(\beta\cos\theta)$ as 28.85nm [10,11]. The grade of crystallinity in these nanoparticles was found higher with minimal hump in the background. This information about the average crystallite size is expected to affect the electrical transport and dielectric relaxation significantly [12] as evident from further measurements.

Figure1. The XRD pattern of Fe$_3$O$_4$ nanoparticles.

The variation of real part of impedance (R) with frequency was obtained at various temperatures for Fe$_3$O$_4$ nanoparticles. From figure 2 it is clear that the magnitude of R decreases when temperature increases which corresponds to a thermally activated type of conductivity [13]. At low temperature R increases sharply indicating an insulating behaviour. With frequency the resistance decreases indicating a pronounced capacitive coupling. As the frequency increases the resistance decreases inferring increased inductive coupling. The relaxation or change in resistance was found to be broad
which is a typical feature of semiconducting nanoparticles [14]. With increase of temperature the metallicity in the particles was found to increase.

![Figure 2](image)

**Figure 2.** The variation of real part of impedance with frequency for various temperatures. The inset image shows fit to the modified HN Model.

The analysis of the impedance relaxation processes was done for the inhomogeneous medium with modified HN method of relaxation applied to real part of the impedance (Since R is also a valid response function). It is important to note that the cold pressed powder can be treated as an inhomogeneous medium with discontinuities and defects. Since the HN model was used to represent both symmetric and asymmetric broadening with variation in the values of $\alpha$ and $\beta$ it is a valid choice for this system. It can be expressed for impedance of a medium as a function of frequency,

$$R(\omega) = R_\infty + \frac{\Delta R}{1 + (i\omega\tau)^\beta}$$

where, $R_\infty$ represents the resistance at the high frequency limit , $\Delta R = R_s - R_\infty$, $R_s$-static resistance and $\tau$ is the characteristic relaxation time.

Relaxation time $\tau$ is calculated from modified HN fit. $\tau$ value was found to be higher at lower temperature i.e., the frequency of relaxation is smaller, which means the electron cluster is tighter at these temperatures inferring the formation of charge ordered areas in the sample. It was realized that the broadening of the AC resistance with frequency increases indicating the loss of cluster area with increase in temperature. A sharp jump in the relaxation was observed at 30 K as shown in figure 3 indicating possibility of a blocking process in the partial volume of the nanoparticles [15]. It is interesting to note that the bulk resistance of the solid does not pick-up the feature of blocking whereas relaxation time does. It is essential to observe a magnetic transition being picked by an electrical transport measurement as indicated in this case. This could be equally a possibility of magnetoelectric coupling in the solid across the blocking temperature. It is known in literature that the magnetoelectric coupling can be seen in Fe$_3$O$_4$ like ferromagnetic solids across the phase transition which may involve a structural change as well as magnetic order change like spin glass [16]. The slow relaxation processes involving clustering and de-clustering of spins in low dimensional solids also can be investigated by this method [2].
Figure 3. Relaxation time ($\tau$) obtained from HN fit of the resistance plotted against temperature

$\tau$ is maximum at the lowest temperature above blocking, it decreases gradually when temperature is increasing and attains minimum at room temperature. This indicates melting of charge order and increased electron ion scattering with temperature in the solid. The drastic change in slope of the relaxation time with temperature [16] is attributed to insulator metal transition in the solid.

Figure 4. The variation of imaginary part of impedance with frequency for various temperatures. The inset image shows fit to the modified HN Model.

To pick up the dissipative processes in the solid the reactance or imaginary part of the impedance ($X$) is measured for any inhomogeneous medium. The variation of $X$ with frequency at several chosen temperatures is shown in the figure 4. Wideness of the reactance peak indicates distribution of relaxation times in this material [13]. The decrease of reactance magnitude when temperature increases, suggests a thermally generated carrier contribution to electrical conductivity. Here, reactance decreases gradually with frequency. This is a clear indication of the capacitive response of the sample which depends on both temperature as well as nature of the material (internal electrical environment). Since $\tau$ is the time between two collisions, at high temperature, a kind of ballistic transport occurs as electrons are moving with very long distance collisions. It’s a typical feature of any low dimensional system. Furthermore, one can notice a kink in relaxation time at about 30K obtained.
from reactance data supporting the possibility of blocking behaviour at low temperature in a selected part of the sample volume. It is interesting to observe a discontinuity in relaxation time across the $T_v$. The fact that reactance can pick up the dissipative processes better compared to the bulk resistance is evident in this observation shown in figure 5.

![Figure 5](image5.png)

**Figure 5.** Relaxation time ($\tau$) obtained from reactance with respect to temperature

The slope change is seen across the $T_v$ with a peak-like behaviour corresponding to a significant electric coupling to the other properties like structure or magnetization.

![Figure 6](image6.png)

**Figure 6.** Variation of resistance with respect to temperature plotted for three different frequencies and the inset image is the variation of conductivity with temperature fitted with an Arrhenius model.

The temperature dependence of electrical resistance with different frequencies is studied from 10-273 K. The decrease in resistance with the increase in temperature indicates the insulator-metal transition (Verwey transition) and the transition is pronounced in the range of 120 K. We have found the activation energy ($E_a$) using the Arrhenius equation, by fitting the log $\rho$ versus $1/T$ i.e.

$$\rho = \rho_0 e^{\frac{E_a}{KT}}$$
where $k_B$ is the Boltzmann constant. Here the relaxation has the thermal activation with a barrier height of $E_a$[17]. The activation energy increases with increasing frequency as shown in figure 6. The fit for the selected frequency is shown in the figure. For this, $E_a$ above Verwey was 56.79meV and 6.17meV below $T_v$. For bulk Fe$_3$O$_4$ activation energy is supposed to be close to 62.2 meV [18] above $T_v$ which supports our observation. The increase of activation energy with frequency shows the coupling of electromagnetic radiation with the charge clusters in the inhomogeneous medium resulting in higher activation energy or local increase of barrier height above $T_v$.

![Figure 7. Variation of DC resistivity with temperature.](image)

The DC electrical transport behaviour of bulk Fe$_3$O$_4$ was investigated in the temperature range of 10-273 K. log($\rho$) vs 1/T curves plotted and the results were fitted to the general expression of activated transport to understand whether the conduction regime corresponding to a semiconductor or to a disordered metal [6].

$$\rho = \rho_0 \exp\left(\frac{T_m}{T}\right)^n$$

where $\rho_0$ is a constant that depends on the phonon density, $T_m$ corresponds to Mott characteristic temperature related to the hopping barrier of the localized states. The exponent $n$ decides the dimensionality (D) of transport in the system using the relation $n = \frac{1}{D}$, the values of $n$ are 1/2, 1/3 and 1/4 for 1D, 2D and 3D respectively[19]. In the present work the transport is divided into two regimes. The first with power $n=0.5$ in the temperature range 170 to 270 K where the dimensionality of transport is 1D the collective charge transfer being Shklovskii and Efros VRH [19]. Further in the low temperature range from 10 K to 120 K the dimensionality was not well defined because of clustered regions of charge order imposed with physical inhomogeneity in the solid.

4. Conclusion

We establish Shklovskii and Efros VRH kind of transport in the cold pressed inhomogeneous Fe$_3$O$_4$ above $T_v$. The relaxation time was found to be higher at lower temperature indicating formation of charge clusters in the insulating phase. The increase of activation energy with frequency indicates coupling electromagnetic radiation with the charge cluster producing higher electron scattering. The reduction of impedance with temperature infers the melting of charge order at higher temperatures. The relaxation time change with temperature supports the observation of charge order melting. The study provides insight into the charge transport mechanism in the physically inhomogeneous medium with magnetic, electrical as well as structural phase transitions specifically in Fe$_3$O$_4$ which is very important for spintronics.
5. References

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