مجلة جامعة تشرين للدراسات والبحوث العلمية _ سلسلة العلوم الأساسية المجلد (23) العدد (10) 2001

Tishreen University Journal for Studies and Scientific Research-Basic Science Series Vol (23) No (10) 2001

Study the Structural Phase Transformation of $(CH_2)_6(NH_3)_2Fe(II)Cl_4$ Compound by Applying Mossbauer Effect and Also by Dielectric Constant Measurements.

J. K. Mulhem*

M.F. Mostafa**

(Accepted 12/9/1999)

□ ABSTRACT □

Mossbauer effect measurements of hexane- diammonium- ferro- tetra- chloride which will be designated as HDFC over the temperature range 311-360 K for single crystal absorbers have been carried out. The behavior of Mossbauer parameters as a function of temperature shows a strong anomaly at 348 K which indicates structural phase transformation.

Dielectric constant measurements of the above compound from 80-380 K at different selected frequencies 60-20000 Hz also have been carried out. The curves obtained by drawing of dielectric loss tand as a function of temperature show a peak at the same temperature of that of the Mossbauer effect where Mossbauer parameters indicated anomalous behavior.

Finally the values obtained for logarithmic real part of dielectric constant Ln $e^{¢}$ are ranging from 3.7 to 5.4 which are typical values for existence of rotational motion. So, the curves of Ln $e^{¢}$ as a function of temperature show a peak. It can be noticed that with increasing frequency the peak is still clear and there is no shift in its position by increasing temperature.

These results confirm without any doubt that there is sructural phase transformation of the mentioned compound happened at 348

***Prof Department of Physics-Faculty of Science- University of Tichreen-Lttakia, Syria**

**Prof Department of Physics-Faculty of Science- University of Cairo,Egypt.

مجلة جامعة تشرين للدراسات والبحوث العلمية _ سلسلة العلوم الأساسية المجلد (23) العدد (10) 2001

Tishreen University Journal for Studies and Scientific Research-Basic Science Series Vol (23) No (10) 2001

دراسة تحول الطور البنيوي للمركب $(CH_2)_6 (NH_3)_2 Fe (II) Cl_4$ باستخدام مفعول مسباور وأيضا بإجراء قياسات على ثابتة العزل الكهربائية

الدكتور جهاد كامل ملحم*

الدكتورة مهجة فريد مصطفى**

(قبل للنشر في 1999/9/12)

□ الملخّص □

أجريت قياسات على مركب هكسان- ثنائي أمونيوم- رباعي كلور الحديد الذي نرمز له اختصارا HDFC *باستخدام مفعول مسباور ضمن مجال درجة حرارة يتراوح بين* 311 *و* 360K *من أجل عينات ماصة أحادية- البلورة. أظهرت وسطاء مسباور بتابعية درجة الحرارة شذوذا قويا عند درجة الحرارة* 348 K *مما يعني تحولا في الطور البنيوي.*

كما أجريت قياسات على ثابتة العزل الكهربائي لمركب السابق في درجات الحرارة نفسها وعند تواترات (ترددات) مختلفة تتراوح من 60 *إلى* 20000 Hz.

تعطي قيم فقد العزل الكهربائي tan d *التي حصلنا عليها بتابعية درجة الحرارة منحنيات كل منها ذروة عند درجة الحرارة نفسها التي أبدت فيها وسطاء مسباور شذوذا في سلوكها.*

أخيرا، فإن القيم التي حصلنا عليها من أجل لوغاريتم الجزء الحقيقي لثابتة العزل الكهربائي Ln e¢ *تتراوح بين* 3.7 *و* 5.4 *هي قيم نموذجية تدل على وجود حركة دورانية. يتضح من هذه المنحنيات أنه مع ازدياد التواتر تبقى الذرى واضحة كما لا يحصل انزياح في مواضعها مع ازدياد درجة الحرارة.*

هذه النتائج تؤكد بما لا يقبل مجالا للشك وجود تحول في الطور التركيبي للمركب المذكور عند الدرجة 348 K.

---

*أستاذ في قسم الفيزياء –كلية العلوم- جامعة تشرين- اللاذقية سورية.

**أستاذة في قسم الفيزياء –كلية العلوم- جامعة القاهرة مصر.

Introduction:

Interest in pervoskite- like systems of low dimensionality was particularly focused on their magnetic behavior [1]. Among such systems are the family of alkylammonium and alkaline ammonium Fe [II] halides, which have been studied expensively in many laboratories [2-5]. These compounds show canted spin antiferromagnetic interaction in the corresponding Mn (II) and Zn (II) have been reported both at high and low temperatures [6-10].

The alkylammonium or the alkaline ammonium chains are located in between the pervoskite layers formed of corner-sharing MCl_6 octahedral, M is a divalent transition metal ion like Fe, Mn, Zn, Co, but in this paper M refers to iron (Fe) because Mossbauer effect is available to this element alone among transition metals. In the cavities between these octahedral the NH_3 groups form N-H Cl hydrogen bonds linking the organic chains to the metal layer. The interlayer bonding is achieved by means of coulomb interactions and Van deer Walls force between the CH_3 groups. The structural transitions in these compounds are a result of the reorientational or conformational motions in these substituted ammonium chains, coupled to tilt the MCl_6 octahedral.

Recently Mossbauer effect measurements on $(CH_2)_6$ $(NH_3)_2$ Fe (II) Cl_4 a member of the alkaline family showed discontinuous variation of the quadruple splitting in the temperature range 200-240 K and it was attributed to possible structure phase change at 235±5 K [11]. Thus it is interesting to study the electric properties of this compound especially around this temperature range.

In this work, we shall present experimental results on the dielectric constant of the above-mentioned compound, which will be designated as HDFC using electrical method. On the other hand, by applying Mossbauer effect spectroscopy, it is possible to conclude by comparison between data of both methods the nature of result transition.

Experimental Procedure:

Crystals of HDFC compound was prepared by dissolving equimolar amounts of 1,6- hexane diammonium chloride salt and freshly prepared ferrous chloride in aqueous solution under a steam of oxygen- free nitrogen gas. Upon heating the mixture under N_2 atmosphere for about one hour and then cooling slowly, greenish yellow crystallites precipitate out. The samples than washed with a mixture of ether and alcohol in 3:1 ratio than dried under vacuum.

The study of recoilless nuclear resonant absorption is more commonly known as Mössbauer spectroscopy. The Mössbauer effect is of fundamental importance in that it provides a means of measuring some of comparatively weak interactions between the nucleus and the surrounding electrons. The Mössbauer spectrum is the transmitted gamma-quanta as a function of Doppler- velocity.

Mössbaure parameters are:

- Isomer shift or center shift (C.S) which appears as a shifting of spectral line from zero

velocity.

- Quadruple splitting (Q.S) resulting as two resonance spectral lines, usually called quadruple doublet.
- Recoilless fraction or Mössbauer probability (f) can be measured as the area under the resonance curve.
- Line width (Γ) is the full width of the transition spectral line at a half maximum.

The Mossbauer absorbers were prepared by using both single crystals and/or powdered crystals mixed in Apiezon grease so they would not settle when placed in a Mylar sample holder. The holder was sealed to restrict oxidation. A 20(m Ci) Co^{27} in Rh source (at room temperature) was used. The velocity calibration was performed using both Fe foil and Na_2 (Fe CN). $6H_2O$ powdered crystals. Fig.1 shows a block diagram illustrating the principle of a Mossbauer spectrometer, while the Fig.2 shows the calibration Mossbauer spectrum of iron.

For measurements the dielectric constant of the sample, a circuit shown in Fig. 3 was used. The current I passing through the sample is calculated from the potential V_R between the terminals of a pure resistance R by the formula:

$$I = \frac{V_R}{R}$$

The value of R was chosen to realize that $V_R << V$ (V voltage between the terminals of the sample).

The dielectric constant ε of the sample at angular frequency ω is calculated by using the relation:

$$\varepsilon' = \frac{11.3\ cd}{A}$$

Where c is the capacitance of the sample (parallel-plate condenser) in PF,d is the thickness of the sample in cm and A is the area of the sample in Cm^2.

The capacitance is calculated by using the relation: $C = \frac{I \sin\phi}{\omega V}$

ϕ : Is the phase angle between I and V in the sample. ϕ and I were measured by a Lock-in Amplifier [12]

Experimental results and discussion:

Mossbauer Effect measurements.

A representative of Mossbauer absorption spectra of the powdered sample between 311-360K are shown in Fig.4.The graph shows a well qoudruple doublet , the data were fitted using the computer program Moss 90 . The value of Mossbauer effect parameters are shown as fuction of temperature at Fig 5 . The line width (Γ) of γ-ray shows a strong anomaly at 348K, also the center shift (C.S) shows a slight increase at the same temperature or plateau of the same temperature. The quadruple splitting (Q.S) shows a region of constant value or plateau of the

same temperature. The area of spectrum Ln A reveals the same behavior. It is to be noted that a small anomaly also seen near T equal nerarly 333K, but it is of much less magnitude. These observed anomaly can be interpreted in terms of structural phase transformation.

Dielectric constant measurements

Electrical measurements determine e' and e'', the real and imaginary parts of the complex dielectric constant. They are frequency dependent and represent the changing and the loss current respectively. The ratio e''/e' is known as the loss (tan d), given by:

$$(\tan d) = e''/e' = \frac{1}{(\tan f)}$$

Fig.6 shows the dielectric loss, which has a peak at the same temperature as that of the Mossbauer effect. The graph attained at 60Hz shows a strong dispersion beyond the peak, which is probably due to DC conduction of the terminal electrodes.

However, the peak is still clear as ¦ (Hz) increases with no shift in the peak's position with increasing temperature. This confirms without any doubt that the transition is of structural nature.

Fig. 7 which depicts Ln e versus T at different frequencies indicates a rotational type transformation. The use of Ln e from 3.7 to 5.4 is typical for rotational motion. Thus we predict that the rotation of the: NH_3- C– C– C – C – C – C – NH_3

ion is behind the observed behavior of the dielectric constant. It is known that this rotational motion is related to the hydrogen bonds present in the compounds.

Finally the experimental results of Mossbauer Effect and electrical measurements indicate that this kind of layered type compound undergoes other structural phase transformation at 348K, and this means that the compounds of perovskite-like systems may be have several phase transitions [13].

Acknowledgment

The author is grateful for support given by the Department of Physics in Faculty of Science – Cairo University- Giza- Egypt.

Fig.1: Block diagram illustrating the principle of a Mössbauer spectrometer.

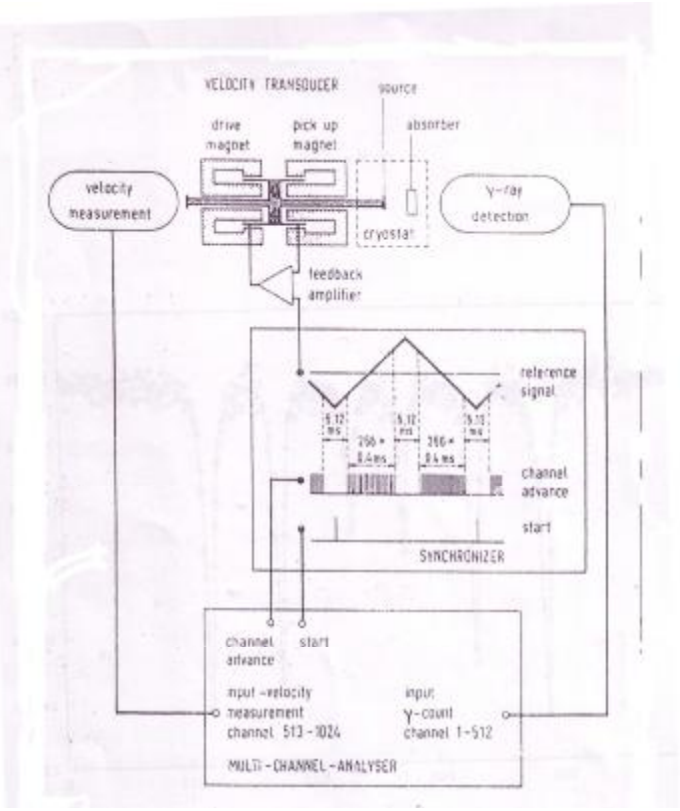


Fig.2: Fe- Calibration spectrum using Fe foil and Na2 (FeCN). 6H2O powdered crystals.

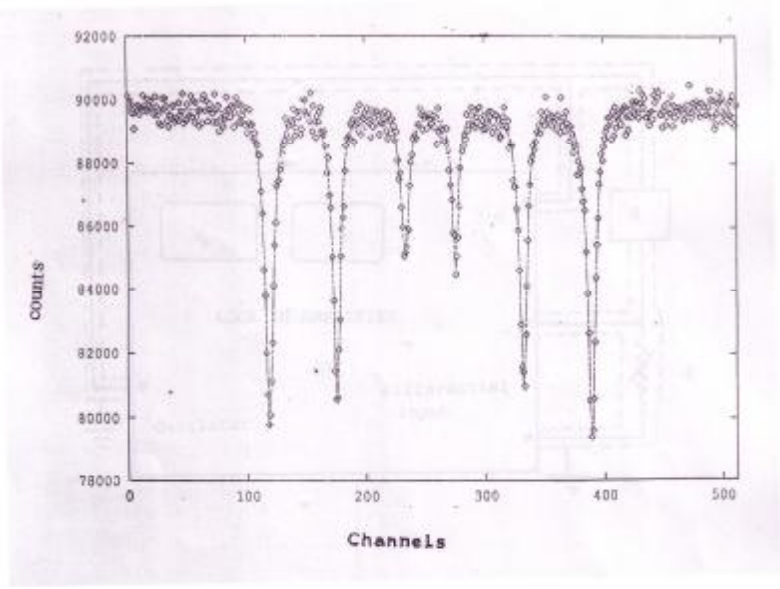


Fig.3: The circuit diagram for the dielectric constant measurements.

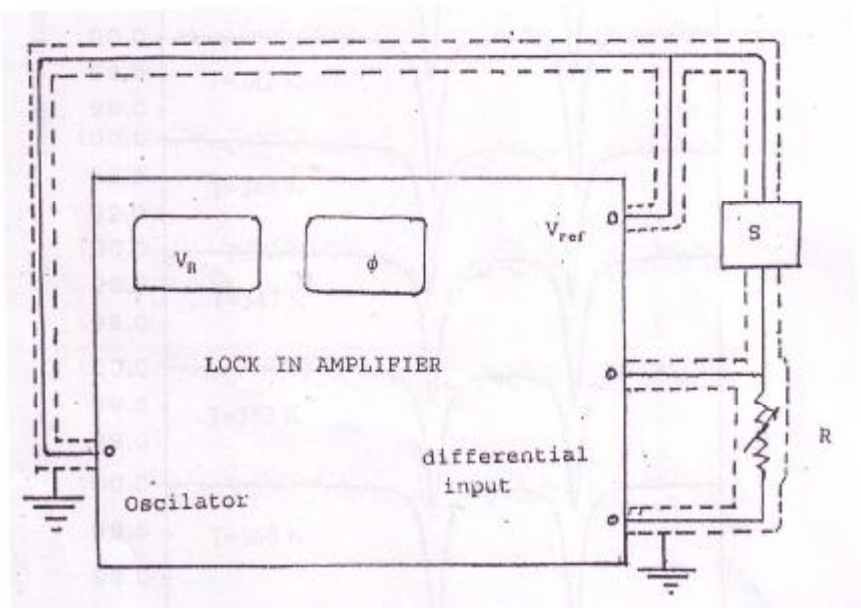


Fig.4: Mossbauer absorption spectra recorded at 311 K, 326 K, 331 K, 336 K, 342 K, 345 K, 347 K, 353 K, and 360 K.

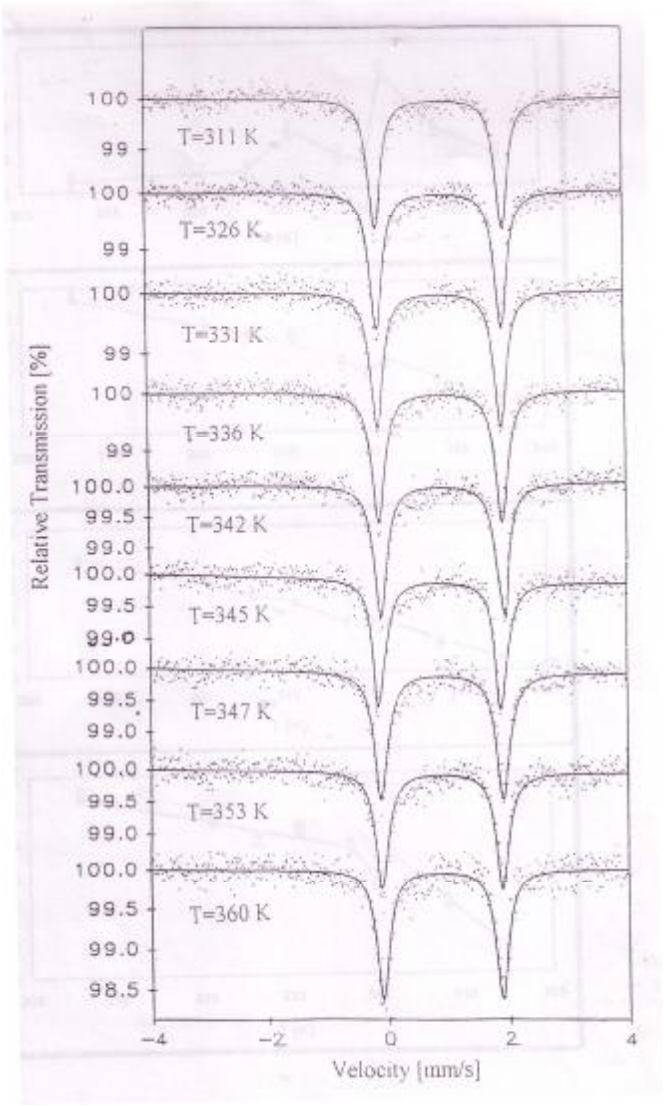


Fig.5: Mossbauer effect parameters as function of temperatures in the range 311-360 K.

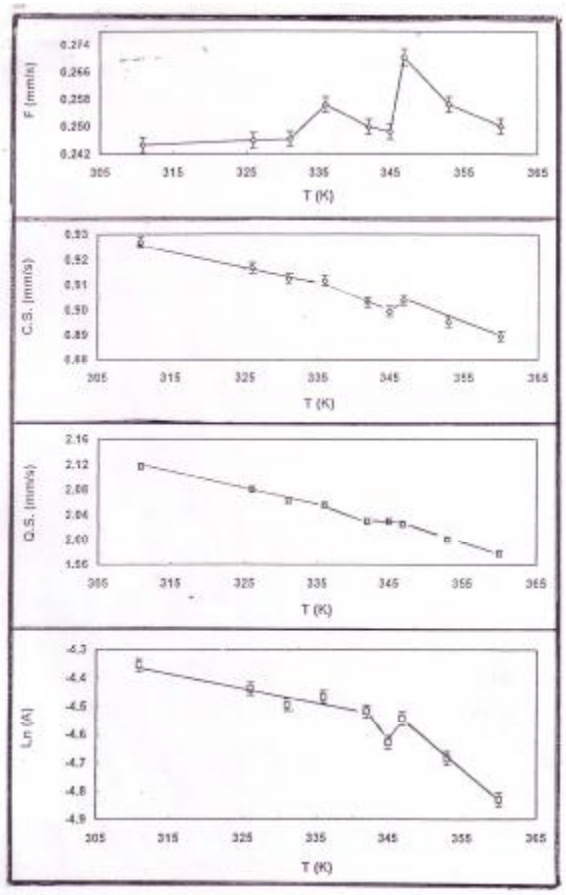


Fig.6: Tanδ as a function of temperature at different selected frequencies between 60- 20000 Hz.

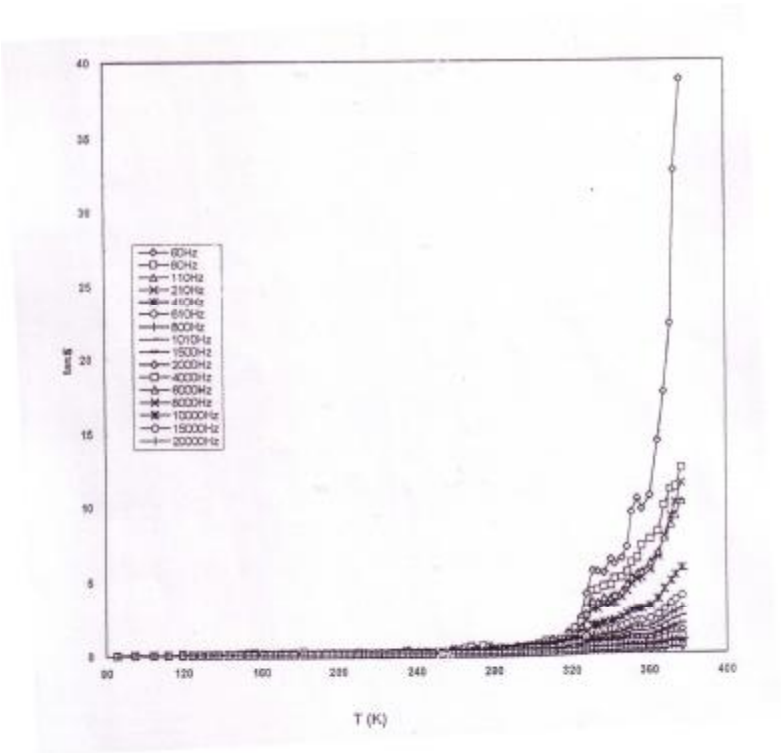
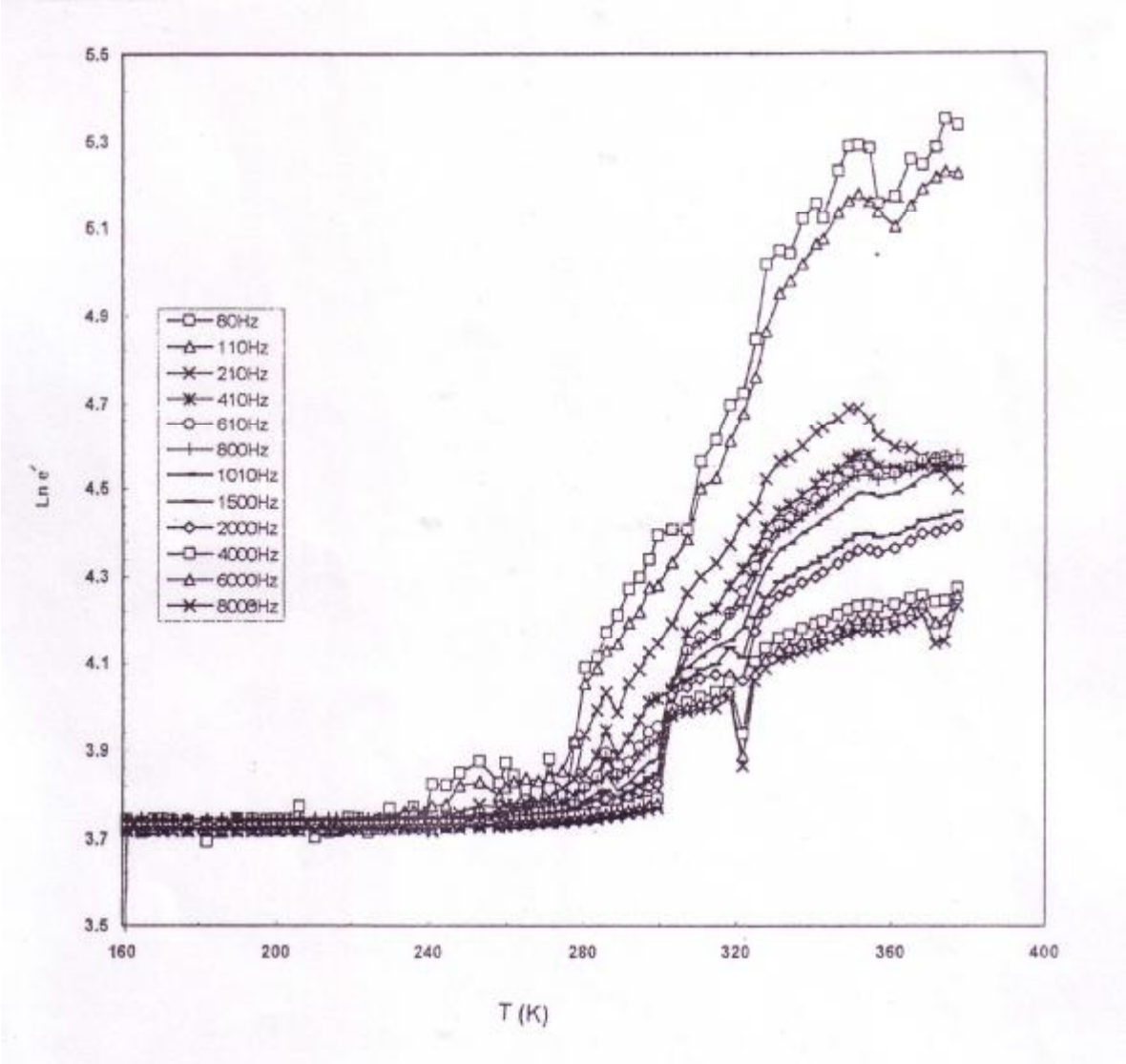


Fig.7: Logarithmic real part of the dielectric constant as function of temperature at different selected frequencies between 80- 8000 Hz.



References:

[1] A.A.ZAKY, R.AWALEY, Dielectric Solids, Routledge and Kegan Paul Ltd. London (1970).

[2] H.FROHLICH, Theory of Dielectrics, Clarendon Press, Oxford (1958).

[3] B.C.CHOI, J.B.KIM and J.N.KIM, Solid State. Comm. 84, 1066 (1972).

[4] A.K.JONSCHER, Dielectric Relaxation in Solids, Chelsea Dielectric Press LTD, London (1983).

[5] S.R.ELLIOTT, Adv. Phys., 36, 135 (1987).

[6] A.R.LONGH, Adv. Phys., 31, 553 (1972).

[7] M.POLLAK, G.E.PIKE, Phys. Rev. Lett., 28, 1449 (1972).

[8] G.E.PIKE, Phys. Rev. B,6, 1572 (1972).

[9] L.J.DE JONGH, A.R.MIEDEMA, Adv. Phys. 23, 1 (1974).

[10] T.MORIYO, Phys. Rev. 117, 635 (1960).
[11] M.F.MOSTAFA, R.M.EMRICK, Phys B210, 67 (1995)

[12] H. Ismael, M.K.ElNimr, A.M.Abou ElAta, M.A.El. Hiti, M.A.Ahmed, A.A.Murakhowsku, Jornal of Magnetism and Magnetic Materials 150, 403 (1995).

[13] M.F.MOSTAFA, A.S ATALLAH and J.K.Mulhem to be published in Solid State Ionic, University of Pennsylvania, USA (1999).