Chapter I An Introduction to ferrites

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CHAPTER I

AN INTRODUCTION TO FERRITE

1. INTRODUCTION

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Magnetic materials and compounds have attracted much attention due to their structural and magnetic properties. These have wide applications and this has become the subject of a tremendous interest to physicist and chemists. These materials continue to attract the attention of research workers because of applications as electronic and magnetic potential ceramics. The technological importance of magnetic gauged from can be the spectrum materials of Magnetic materials are of different applications. types, such as, ferromagnetic materials, hexaferrites, magnetoplumbite magnets, alloys, oxides etc. Of these hexagonal ferrites are considered to be the most significant materials due to their specific electrical and magnetic properties.

Lodestone (FeOFe₂O₃) is first natural occurring ferrite. The systems $BeO - MeO - Fe_2O_3$ have became of recent technical interest, due to their high quality magnetic behaviour. The simultaneous requirement of optical, electronic and magnetic properties in the advanced electronics, and microwave, and computer technologies have focussed the attention of scientist

on magnetic materials, viz. the family of Barium ferrites and substituted magnetoplumbites.

The technological importance of ferrites can be gauged from the spectrum of the application in high frequency and pulse transformer, inductances, deflection coils and other applications depending on the requirements of high permeability and low loss at high frequencies. Ferrites with square 1000 characters of B-H curve, find extensive use in computer memory as core devices.

During the last two decades a substantial to prepare the ferrite materials to fulfil the qualitative as well as quantitative demand in electronic and telecommunication technology. Fig.1.1 shows the spectrum of applications of ferrites as a ferrite tree (20).

1.2 HISTORICAL

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During 600 BC Greeks reported magnetism in the mineral loadstone(Magnetite) which is the first ferrite.

About 1000 A.D first application came out, mariners used lodestone in compasses. The modern period with the work of Snoek (1947) and then the development of ferrite material started as outlined significantly in Table (1.1).



Table 1.1

Scientist	Area	Sigificance R	ef.
Hilpert	Synthesis of ferrites	Success to reduce 2 losses in inductor of transformer	
Kato, Takei, Barth, Posjank	Magnetization and other views	The structure of ferrites was established to be spinel type 3,4	,5
Snoek	Preparation & Magnetic prop.	Developed commercialy 6 usefull Ferrites	,7
Veruay	Electrical properties	Established the reason of electronic conductivity in ferrites	8
	Crystal stru- cture	Shows inverse structure ferrites are ferrimagnetic & normal spinel structure are non-magnetic	
Nee 1	Spin - spin interaction	Provide a theoratical key & introduce the concept of mag. sub-lattice	7, 10
Anderson & Vanvieck	Basic inter- actions	Developed theory of super- exchange interactions	11
Yafat & kittle	Theory of mag. sublattices	Formulate theory of a "triangular" arrangment of three sublattices	12
Gorter & Guilland	Magnetization	Gave direct expt. proof of Neels theory	13 , 14
Smorter & Gorter	Magnetisation & microwave resonance	Corelated independantly th cation distribution 1	e 5,16
Shull & Strauser	Neutron deff- raction	Confirm Neel's theory for Magnatite & Zn-ferrite	17

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A. Salar

مقدوب ويتبته وعاسر بسطار عنامه علميه ويربله وإينية مدينة بالمائية مقامة معادي متباية وعنها با	ماله منه بلغه بينه بلغ يحد بلغة عنك بقته العرب تعاد عنه بلغة بينه عنه الع	
Gilleo	Magnetisation	Corelate Curie temperature 18 with cation distrubution & magnetisation
Koops	Conductivity	Gave phenomenological theory to explain conductivity behaviour

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1.3 CRYSTAL STRUCTURE

The magnetic oxides exhibit the following the structures in general.

- 1. Hexagonal structure
- 2. Magnetoplumbite
- 3. Spinel and perovskite structure
- 4. Garnet structure.

1.3.1 Hexagonal structure

Higher oxides with large molecular weight are found to exhibit magnetic behaviour similar to spinels, these are also called hexagonal ferrites, due to their crystal structure. The cubic and tetragonal ferrites have spinel and distorted spinel structures with general chemical compositions as XY_2O_4 .

The hexagonal structure has chemical formula MFe₁₂O₁₉ where M can be Ba, Sr, Ca. Fe ion may be substituted by Al or Ga ions. Hexaferrites have attracted great attention as they have significant applications in industry, as magnetic recording media and isolators etc. Some of the typical examples of each type are : BaFe¹¹¹₂O₄ (B), BaFe¹¹¹₂O₁₉ (M), BaMe¹¹₂Fe¹¹¹₁₀O₂₇ (W), Ba₂Me¹¹₂Fe¹¹¹₁₂O₂₂ (Y),

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 $Ba_{4}Me^{xx}_{2}Fe^{xxx}_{36}O_{69}$ (U). These are referred in short as B, M, W, Y, Z, X, and U respectively (Braun 1957).

The system BaO - MeO - Fe₂O₃ and SrO - MeO - Fe₂O₃ have become important due to their high quality magnetic behaviour (Rathenau 1953, Coehart 1963, Saure et al 1978, Ram 1989, Sato et al 1990). The compounds of the system MO - Fe₂O₃ - Ba₂O₃ (M = Ba, Sr, Cu, and Pb) on the other hand are useful as glass ceramics. The generally quoted ferromagnetic compounds of the type LaMeFe₁₁O₁₇, where Me represents Co, Ni, Mg, Cd, Cu, or Zn have also been reported by V.N. Mulay (1970) as hexaferrites.

Structure Details :

The structure of these ferrites have been mentioned as closely packed oxygen ions, built up of layers of cubic and hexagonal stackings alternately. The structure has cubic blocks which have their triad axis (111) parallel to the c - axis, coupled by hexagonal blocks containing the separate Oxygen, Barium layers. The Fe³⁺ ion may be located in three different sites octohedral, tetrahedral and bipyramidal sites.

In the hexagonal structure only one metallic ion available, for two adjacent tetrahedral sites, which occupies intermediate position along claxis.



1.3.2 Magnetoplumbites (Hexagonal Ferrites)

In case of cubic ferrites, substitution of Fe^{3+} ions is possible by some suitable ions, the common term spinel, rather than ferrites, appears to be mere appropriate. Similarly substitutions of Pb^{2+} , Ba^{2+} or Fe^{3+} cations are called as magnetoplumbites even in the absence of plumb, if it crystalize in M - structure, all such compounds are shortly called M - ferrites.

The ferrimagnetic oxides having a structure similar to the mineral magnetoplumbite PbFe7.sMn3.sALe.sTie.sO19 are referred to sometimes as hexagonal ferrites. The permanent magnet material BaFe12019 referred as Ferroxdure is an often quoted magnetoplumbite example of structure. The magnetoplumbite compounds also have hexagonal structure and their chemical formula is XBaO:YFe₂O₃:ZM+²O where M is a transition metal. They are best examples of permanent magnetic materials. This type of compounds were extensively studied by Jonker et.al(24). Several ferrimagnetic oxides have also been discovered, (Table 1.1). These materials have a large magnetic Ferroxdure has an external anisotropy anisotropy. field of 17,000 gauss. This type of materials be have otherwise very much like a ferrite with a Neel μ_{ij}



temperature of 468° C and maximum magnetization of 4715 gauss (Lox & Button 1962).

The chemical composition diagram Fig.(1.4) and Table+3.1.3 illustrate the close relationship between these compounds and the ferrite spinels denoted by S. These compounds S, M, W, Y and Z appear in the composition diagram near the apex. Fe₂O₃, we should expect they posses analogous magnetic properties as found in - ferrites. This is attributed due to the presence of the Fe³⁺ ions in tetrahedral and octohedral sites. The long anisotropy however arises because of the existence of the large barium ion and the slight alternation of structure in the neighborhood of the barium ion.

1.3.2.1 The mixed Cubic - Hexagonal crustal structure

A large portion of the M structure viz Barium ferrite, is identical to the spinel, where the oxygen ions are arranged in a cubic close - packed lattice with the metal ions in the interstices [Fig.1.5], exhibits in every fifth layer of oxygen ions in the structure M, there appears one barium ion in place of oxygen ion. This layer is denoted by "Barium layers". The shaded portion denoted by "Dxygen - 4" containing four oxygen layers, are the same as the cubic spinel S structure. The difference between the hexagonal close -



Table 1.2

Symbol	l No.of Mol. per/unitcell	Chemical	formula	Con MeO	Ba0	(mo1%) Fe ₃₀₃
8		MeO.Fe ₂ O ₃	(MeFe ₂ 0 ₄)	50	-	50
т		Ba0.2Fe ₂ 0 ₃	(BaFe ₄ 0 ₇)	-	33.33	66 .6 7
в		BaO.Fe ₂ O ₃	(BaFe ₂ 0 ₄)		5 0.0 0	50.00
M	2M	Ba0.6Fe203	- unit, alter olen aller aller user sitte blav at	44 - 44 - 44 - 44 - 44 - 44 - 44 - 44	14.29	85.71
		(BaFe12019	•)			
W	2MeW	2MeO.Bao.e	Fe203	18.18	9.01	72.71
		(Me ₂ BaFe ₁₄	.027)			
Y	3MeY	2Meo.zBao.	"Fea03	20.00	20.00	60.00
		(MeaBaaFea	2022)			
Z	2MeZ	2Мер.зВар.	12Fe203	11.76	17.65	70.59
		(Me_Ba_Fe	200 (A do)			
x	3MeX	2Meo. 2Bao.	14Fe203	11.11	11.11	77.78
		(MeBa ₂ Fe ₂₀	904 <u>4</u>)			
U	MeU	2Meo. 4Bao.	10Fe203	8.37	16.57	75.00
		(Me ₂ Ba ₄ .Fe	?360 60)			

M - type and other hexagonal compounds

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Table 1.3

Compound	Composition	Interelation
S	Me ²⁺ Fe ₂ 0 ₄ or MeOFe ₂ 0 ₃	
м	Pb0.6Fe203	
	$BaFe_{12}O_{19}$ or $Bab_{0.6}Fe_{2}O_{3}$	
ω	BaMe2 ²⁺ Fe16027 or	W = M + 28
	BaO2Me _{e.e} Fe ₂ O ₃	
Y	Ba2.Me ²⁺ Fe ₁₂ 0 ₂₂	
	2Bao.2Meo.4Fe203 or	
z	Ba3Me2 ²⁺ Fe24 O41 or	Z = M + Y
	38a _{0.2} Me _{0.1} 2Fe ₂ 0 ₃	

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packed structure, in the neighborhood of the "Barium" layers and the spinal S cubic close packed structure elsewhere lies in the arrangement of metal ions in the interstices.

We can examine this by considering the environment of the oxygen ion marked 0 in the Barium block. The position of neighbouring oxygen ions in horizontal plane are generated by two 120° rotations, one forward, one backward, about the vertical axes of three fold symmetry.

In the Fig.1.5 there is a metal cation C located above the oxygen plane and another an equal distance below. If, however, we choose the oxygen ion O' in the "oxygen -4 block", the oxygen ions nearly have the same symmetry, but the cation layers above and below are not identical. The metal cations now occupy three types of sites. These are octohedral sites (open dircles) and tetrahedral sites (black dots) as in spinel. In addition, the single ion (double circle) to the left of O is the Barium layer occupies a new type of site.

This latter ion is Fe^{3+} surrounded by five oxygen ions i.e one metal ion between two tetrahedral sites. These abnormalities in the "Barium layer" result in a preferential direction of magnetization along the z-

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1.3.2.2 The Superexchange Interaction in M - Ferrites

It has been shown that (Gorter 1954) the magnetic properties of those oxides are due to the ferrimagnetic interactions. The superexchange interaction in M compounds is shown in Fig.1.6.

The superexchange interactions for $Fe^{3+} - O - Fe^{3+}$ in magnetoplumbites are strong and negative when the angle through the intervening oxygen ion is near 180° and when the distances of closest approach are relatively small.

The three metal ions surrounding O shown in Figure 1.6. The angle $Fe^{3+}(3) = 0 - Fe^{3+}(2)$ is 140° and angle $Fe^{3+}(2) - 0 - Fe^{3+}(3)$ is 80°. Therefore the superexchange interaction between 2 and 3 is negligible. Both 2 and 3 align antiparallel to 1. Ion $Fe^{3+}(3)$ is turn, is coupled to the "oxygen 4" block by strong negative interaction $Fe^{3+}(3) = 0 - Fe^{3+}(4)$. alignment of ions 3 and Therefore, the 4 are antiparallel. The interaction $Fe^{3+}(1) = 0 = Fe^{3+}(4)$ does not compete effectively because the distance of No. 1 from the intervening oxygen ion is about 2.5 A° compared with a typical interaction distance of about 1.3 A-.

The superexchange interaction in the neighbourhood or the barium layer accounts for the uniaxial



anisotropy of Ferroxdure along the c axis. Since the cubic spinel block has no strongly preferred axis of alignment, the coupling from the barium layer impose its strong preferential orientation on the spinel block.

5 µB to the magnetic Each Fe³⁺ ion contributes moment at absolute zero, and we may form an algebraic sum of the contributions to determine the saturation magnetization. The twelve Fe³⁺ ions of the formula unit consist of one in the barium layer(up) and two octahedral ions(down) and in the "Oxygen - 4" black, seven octahedral ions(up) and tetrahedral ions(downs). The total is 5 μ B x (1-2+7-2) = 20 μ B. This value is in excellent agreement with the corresponding experimental measurements of magnetization at very low temperatures. The superexchange interaction scheme which produces the unique temperature dependance of the magnetization.

The resultant magnetic moment per unit formula in M - structure is equal to the sum of the seven octahedral ions and the ion in the layer containing barium, reduced by the moments of two octahedral and two tetrahedral ions, which are oppositely oriented to them. Directions of the magnetic moments given in Tables 1.4.

Coordination number	Number of positions	Wyckof's notation	Dir. of Mag. momt.per mole
6	12	k	• • • • • •
(Octahedral site)	4	ť	4 Y
	2	æ	1
4 (Tetrahedral site)	4	f	¥ 4
5 (Tricopal bipyra-	2.	b	4
midal site)			

Table - 1.4

Direction of magnetic moment of Fe ions in the unit

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cell of magnetoplumbite (M).

1.3.3 Spinel Structure

The general chemical formula for the ferrospinel is MFe₂O₄ where M is the divalent metal ion and Fe is trivalent ion. All the compounds of this type have a cubic, face centered crystal structure (Fig 1.7, a,b) of the space group $(O_n^7 - F_3 - O_m)$ with unit cell containing 8 formula units.

In this structure two types of interstitial positions occur with respect to oxygen lattice and these positions are occupied by metal ions. There are 96 interstitial sites per unit cell in all, 64 being tetrahedral and 32 octahedral. Out of these 8 tetrahedral and 16 octahedral sites are occupied by cations. Tetrahedral sites are usually called as A sites and are surrounded by 4 oxygen ions and octahedral sites are called as B sites which are surrounded by 6 oxygen ions. When all the 8 divalent ions occupy the tetrahedral sites and all the 16 trivalent ions occupy the octahedral sites then the structure is called the normal spinel. 14 the tetrahedral sites are occupied by 8 trivalent ions instead of divalent ions and the 8 divalent occupy the octahedral sites along with the remaining 8 trivalent \sim ions then structure is called inverse spinel; \sim_P



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The M - type compounds are similar to spinels, due to the fact that, the interacting orientation of the iron ion magnetic moment in the spinel block of hexagonal ferrite is same as the orientation of the spinel in the ferrites having spinel structure.

Perovskite Structure

The Perovskite structure has a chemical formula $LnFeO_3$ [Fig 1.8]

where Ln may be Y, Ge, Pr, Nd etc. The structure is orthorhombic with space group D_{2h}^{1+} -pbnm. The unit cell contains four group of LnFe₂O₃. In this oxygen ions constitute central cubic blocks with two types of sub lattices. One is dodecohedral i.e. rare earth ion is surrounded by 12 oxygen ions and second one is octahedral i.e. Fe ion is surrounded by 6 oxygen ions. This type of materials have been studied by Geller (20) and Travern (21).

1.3.4 Garnet structure

1.10.1

The natural garnet is grasslarite $Ca_3Al_2(SiO_4)_3$. The most widely studied garnet so far is the yttrium iron garnet having chemical formula $5Fe_2O_3$. $3Y_2O_3$. Garnet structure was fully explained by Bertant (19) and Geller and Gilleo(17).

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The garnet structure is cubic and has a space group D_n^{10} -Ia.3d. The structure has three types of cations sites designed as a,c,d. The metal ion positions, 16a have octahedral, 24c have dodecahedral and 24d have tetrahedral oxygen surrounding. The large Y ions are located in dodecahedral sites and a small Fe ions are located in tetrahedral and octahedral sites. Each oxygen ion has two Y³⁺ ions, are Fe³⁺ ions from A sites and one Fe³⁺ ions from A site as nearest neighbours. In Fig. 1.9, the garnet structure is shown.

The Y ion in YIG formula can be replaced wholly or in part by trivalent rare earth ions substitutionally. This changes the magnetic properties. The Fe ion may be replaced by other trivalent ions which may prefer one of the two a, d sublattices, depending on size and other unknown considerations e.g. Al and Ge prefer tetrahedral sites whereas In and Se prefer octahedral sites.

1.4 APPLICATIONS OF FERRITES

Technological advances in ferrite manufacture and property control have permitted the electronics industry to go far in effectively applying their versatile properties. New applications are constantly being reported.

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The high permeability and high resistivity characteristics of soft ferrites are used in applications such as transformers and chokes. The ferrites are used in high frequency applications, where the use of metallic core is ruled out because of the eddy current losses. Major applications of soft ferrites are as high frequency transformer cores, antenna rods, recording heads, induction tuners etc. In the input circuit of radio receivers, areal rods of various shapes are employed to improve sensitivity. The coil wound on the ferrites is generally used as the input circuit thereby the obviating the need for areal matching, low noise and directional sensitivity are characteristics of ferrite areal.

The use of tubes, rods and screw cores for tuning applications favour in RF the trend towards miniaturization. The important benefits are high Q factors and wide tuning range due to the high permeability. The applications of ferrite is confined to its typical frequency range. Cup cores or tubes of high permeability ferrites shield Rf coils with minimum stray fields. The residual losses increase with frequency. This particular property of ferrites permit $_{\rm eff}$ the use of heads or ferrites tubes for broad band damping in the frequency range 10 MHz to 1000 MHz. In '

order to decrease spurious radiation and to avoid undesired coupling in radio and TV receivers, motors, ignition circuits and convertor, ferrite core broad band chokes are used with advantage.

Some hexagonal ferrites are suitable as permanent magnetic materials because of their high uniaxial anisotropy. The important applications include loud 'speakers, motors, generators, sticking device. A large quantity of oxide magnetic materials is used for magnetic recording purposes. The important characteristics required for this purpose are 1. High remanance and 2. Moderately high coercivity.

The ferrites can be used in magnetic amplifiers as non linear circuit elements. For this purpose ferrites with very small coercive force are to be used which give a sharp kink in the hysteresis curve. Storm(24) and Attura(25) used Mn-Zn ferrites for this purpose in order to get coercive force as low as posible.

Peizomagnetic ferrites can be used in ultrasonic transducers in which magnetic signal is converted into a mechanical vibration. The development of piezomagnetic ferrites has been reviewed by van der Burgtant and Stujjts(26).

In large nuclear particle accelerators the near p_{q} circular path of the charged particles can be obtained

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by the use of guiding magnetic fields. The magnetic design of such huge machine is of great importance and many hundreds of tons of commercial ferrite material has been used in the proton synchrotrons at present in operation. In a accelerating machine named as synchrotron, a ferrite accelerating resonator, is being proposed by Averbukh(27).

1.5 ORIENTATION OF PRESENT WORK

As discussed in earlier sections much work seems to have been done on ferrites in general. The more detailed survey of magnetoplumbites points out that. barium, strontium, calcium and lanthanum (Deschamps et al 1967, Dritenik et al 1973, van Dieten et al 1974, 1978, Mulay et al 1970, Due et al 1983, Borkar 1987) containing M compounds are studied, but correspondingly M-compounds have no detail nickel reference in literature. The ferromagnetic compounds of the types La³⁺Me²⁺Fe₁₁³⁺O₁₉ where Me represents Co, Ni, Mg, Cd, Cu or Zn have been reported by V.N. Mulay(1970) as hexaferrites, but the NiFe12019 will be the nickel ferrite in pure form and the compound in perfect stoichiometry finds no place in the literature. However deviated stoichiometric similar compounds are reported ways (Ichinase et al 1963, Rotgering et al 1980, Yamamoto et al 1979) which indicate that such addition of trivalent

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metal ion such as La^{3+} essential for the formation of the M structure.

Keeping in view the above mentioned work of various scientists, it is proposed to prepare a ferrite $NiAl_{x}Fe_{12-x}O_{12}$ system with variation of Al ions. The interesting electrical and magnetic properties of the samples in the system obtained by us are reported in this thesis.

The samples were prepared by the standard ceramic technique using pure oxide constituents. The necessary instrumentation was fabricated in the Departmental workshop.

After having prepared the ferrite samples of desired composition, the crystal structure characterization was made by x-ray studies. The work on d.c. electrical resistivity and the studies on the cation distribution of the system were reported.

The hysteresis study of ferrites is of importance to estimate saturation magnetization, coercivity and remanant magnetization. Correlative studies of d.c. resistivity and cation distribution were discussed.

Particularly the compounds in which Al³⁺ is substituted for Fe³⁺, Cr³⁺ and Co³⁺, the distribution of cations in different crystallographic positions is easy. This is so since Al³⁺ have large scattering Π.

factor relative to 3d cations. Thus a systematic comparison of Ni ion containing M type compounds forms a significant subject of the present thesis.

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REFERENCES

- 1. Hilpert Ber Deut Chem. Ges.42 2248 (1909)
- Kato Y., Takei, Trans. Am. Electrochem. Soc. 57 297 (1930).
- 3. Forrester H, Vetter M. Compt. Rend 209 164 (1930).
- Barth. T.F W, Posnjack E.
 Z. Krist. 82 325 (1932).
- 5. Snoek J.L. Physics 3 463 (1936)
- 6. Snoek J.L. " New Developments in Ferromagnetic Material" Elsevier Press Inc. New York (1947)
- Verway E.J.W.F.C. Romeijin and E.C. Heilman. J. Chemi. Phys. 15 174, 181 (1974).
- 8. Neel L. Am. Phys. (Paris) 3 137 (1948)
- 9. Neel L. Proc. Phys. Soc.(London) A65 869 (1952).
- 10. Anderson P.W. Phys. Rev 89 350 (1950).
- Yafet Y, Kittle C, Phys. Rev. 87 290 (1952).
- 12. Gorter E.W. Philips Res. Report 9 295 (1954).
- 13. Guilland E. J. Phys. Radium 12 239 (1951)
- 14. Smart. J.S. Phy Rev. 94 847 (1954)
- 15. Gorter E.H. Nature 173 123 (1954).
- 16. Suull C.G, Strauser W.A. A. Phy. Rev.81 483 (1951)

- 17. Gilleo M.A, Geller S. Acta. Crystal 1**9** 239 (1957)
- 18. Koops C.G, Phys. Rev. 83 and 121 (1951)
- 19. Bertaut F, Forrat F, Compt. Rend. Acad Sci Paris 243 282 (1956)

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- 20. Geller S, Acta Cryst. 11 565 (1958)
- 21. Traves D, J. Appl. Phys 36 1033 (1965)
- 22. Kapan T.K Phys. Rev, 129 (1962) (1983)
- 23. Htgweing F.K., Philips Rev. 11 (337) 190 (11956)
- 24. Storm F.H. "Magnetic Amplifiers", Willey, New York (1955)
- 26. Van der Burt C.M. and Stuijts A.L. Development in ferrite ceramics with strong piezomagnetic coupling ultrasonics. 1 199 (1963).
- 27. Averbukh I.J, Insrum and Expt. Tech (USA) No.4 part 21, 848 (1978).