CHAPTER-I

AN INTRODUCTION TO FERRITES

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1.1 Introduction:

The term 'Ferrites' is used to mean magnatic oxide containing iorn oxide as there main component regardless of their crystal structure [1]. The ferrites of greatest technical improtances are derived crystallographyically from three natural compounds namely the spinel, the garnet and the magnetoplumbite. To cater to the quantitative and qualitative demands of the consumer electronics as well as in computer technology, substantial efforts have been made by various laboratories to prepare ferrite metarial sinces last fifty years.These are used for a variety of different applications after designing and tailoring specifically for the purpose[2]. Some applications are found in permannant magnets, ,TV deflection yokes, transformer cores, computer memory and logic devices.

This chapter deals with the fundamental properties, structure and theories of ferrites. The applications of ferrites and orientation of the present work are also included at the end.

1.2 HISTORICAL BACKGROUND:

The naturally prepared ferrites $FeOFe_2O_3$ aroused the scientific curiosity of man. The ancient people living in 600 B.C. believed that load stone(magnetite) possesses an inherent living force which accounts for the observed attraction between magnetic and iron[3]. The first measurment of saturation magnetisation of magnetite was made by DU-Bois (1890) [4] Pierre Weiss (1907) went futher to determine curie temperature and suggested its possible use in reducing eddy current loss in inductors and transformers [5] . However the credit of preparing large number of ferrites with general formula $MOFe_2O_3$, where M is the divialent metal ion ,goes to Hilpert (1909) [6] .

One of the most significant contributions was made by Barth and Posnjak by carrying out x-ray analysis on ferrites . By assuming that divalent and trivalent metal ions interchange positions in crystal , they discovered inverted spinel structure , essential for the existence of the ferromagnetic properties of ferrites .

Philips research laboratories in Eindhoven Holland became the centre of extensive work in ferrites in 1930 and commercial significance was achieved by the work of Snoek [7] and his co-workers . The importance of accurate oxygen content for the quality of ferrite to be used . at high frequency was shown for the first time . Verwey et al [8] reported electronic conductivity of ferrites which is mainly due to the exchange of electrons between Fe^{2+} ions and Fe^{3+} ions in ferrites.

The ferrite with inverted spinel structure was shown to be ferrimagnetic whereas normal spinel structure ferrite to be nonmagnetic. The work of Verwey , Heilman and Romeijn on resistivity supported their conclusion of ferrimagnetic and non-magnetic ferrites [9]

Neel [10-11] published the first explainatory theory on the origin of magnetism in ferrites by introducing the concept of sublattices to explain the spin -spin interachon in 1948 and modified the same in 1952 .Anderson and Vanvleck developed the super exchange theory of interachons [12-13] . Yafet and Kittle [14] suggested the modificahons in the Neel's theory by postulating a triangular arrangement of spins in a sublattice so that net spin of the sub-lattice is opposite in direction to the spin on the other sublattice of ferrite . The experimental proof of Neel's theory was established by Gorter [15] and Guillaud [16] by measuring the magnetization of the mixed ferrites . Shull and Strauser [17] confirmed the Neel's theory for magnetite and zinc ferrite with the help of neutron diffraction studies . The correlation of curie temperature with magnetization and cation distribution was carried out by Gilleo [18] .Koops [19] studied high conductivity associated with high dielectric constant and obtained the formula giving a phenomenological theory to explain the conduction behaviour .

Prof. Takie In I C F (1980) and Hirayam stressed on the use of ferrite material as a power ferrite [20-21] . In the following four years the switched mode power supply market grew rapidly there by increasing the literature on power ferrites. Kamada A and Suzuki[22] and Goldman[23] compared the better performance of power ferrites with comparatively low cost . Since then the power ferrites are extensively used in power supplies operating at 1 MHz and above correspondigly a large number of papers were presented In I C F (1989)

1.3 STRUCTURE OF SPINEL FERRITES:

The crystallographic structure of the cubic ferrites of the spinel type is determined by a closely packed structure of oxygen ions. These are assumed to be rigid spheres of ionic radius r_O^{2-} = 1.38 A°. some of the remaining hollow spheres are occupied by the smaller metal ions with r_{Me} =0.6 to 1.0 A°.

The mineral spinel crystallizes in the cubic system and contains eight formula units of $MgAl_2O_4$ in the unit cell. The spinel ferrites are formed from $MgAl_2O_4$ by substituting Fe^{3+} for Al. Any divalent cation with an ionic radius between 0.6 and 1.0 A° can be substituted for Mg according to the general formula $Me^{2+}\ Fe^{3+}\ O_4$. where Me^{2+} is Mg, Ni, Co, Cu, Fe,Zn or Cd. In the spinel lattic there are two kinds of lattice-sites available for the cations; tetrahedral sites (A sites, surrounded by four oxygen anions which are situated in the corners of a tetrahedron, with only 8 of 64 sites available in each unit cell occupied) and octohedral sites(B sites, surrounded by 6 oxygen anions which are situated in the corners of an octohedron with 16 of 32 sites in each unit cell occupied.)

The model assumed so far needs refinement as oxygen anions are rigid spheres arranged in a close packed structure and hollow space between them are filled with smaller metal ions. the hollow spaces available in an ideal close-packed structure of rigid oxygen anions would be able to incorporate on tetrahedral sites. Only ions with maximum radius r_{tetra}<=0.30 A° and on octohedral sites only ions with a maximum radius r_{oct} <= 0.55 A°. This would result in a cell edge a= 7.47 A° . To Incorporate the cations mentioned above the lattice has to be expanded somewhat . The difference in expansion of the tetrahedral and octohedral interstices is characterised by an oxygen parameter U. For an ideal lattice tetrahedral and octohedral interstices are enlarged in the same ratio. The distance between the tetrahedard site (0,0,0) and oxygen site(3/8, 3/8, 3/8) is $U_{\text{Ideal}} = 3/8 = 0.375$ In incorporating thedivalent cations U_{obs} is larger than U_{Ideal} always, owing to the stronger expansion of the tetrahedral interstices at the expense of octohedral sites. For small displacements, the radii of the ions on tetrahedral sites and octohedral sites r_A and r_B are given by .

$$r_A = (u - 4)\, a\sqrt{3} - r_o^{2-}\ ; \quad r_B = ((5/8) - u)a - r_o^{2-}$$

Regarding the distribution of the divalent and trivalent cations on A and B sites, it might be thought at first that the eight divalent cations are situated on the eight occupied A sites and 16 trivalent iron ions on the 16 occupied B sites (normal spinel). However this does not hold in all cases. Experiments show that there is a whole range of possible distribusions [24] which can be represented in general terms by -

$$Me_{\delta}^{2+}Fe_{1-\delta}^{3+}(\ Me_{1-\delta}^{2+}\ Fe_{1+\delta}^{3+}\ )O_4$$

where the braukei indicates the octahedral sites. the limiting case $\delta = 1$ is called normal spinel and limiting case $\delta = 0$ is called inverse spinel. The case $\delta=0$ should be even more likely because $r_B > r_A$ and $r_{Me}^{2+} > r_{Me}^{3+}$

A completely normal or completely inverse spinel represents an extreme case. X-ray and neutron diffraction studies have shown that there exists intermidiate structure which is neither a perfect normal structure nor a perfect inverse structure. This happens when δ takes any value between 0 and 1. Thus the quantity δ is a measure of the inversion. In case of some ferrites δ depends upon the method of preperation.

The ferrites $ZnFe_2O_4$ and $CdFe_2O_4$ have normal spinel structure and are non-magnetic. $NiFe_2O_4$, $COFe_2O_4$ have inverse spinel structure like that of Fe_3O_4 and are magnetic in nature. Ferrites like $MgFe_2O_4$ have partial inverse spinel structure and they are magnetic.The spinel structure and A-site and B-site arrangments are shown in fig.1.1 and 1.2.

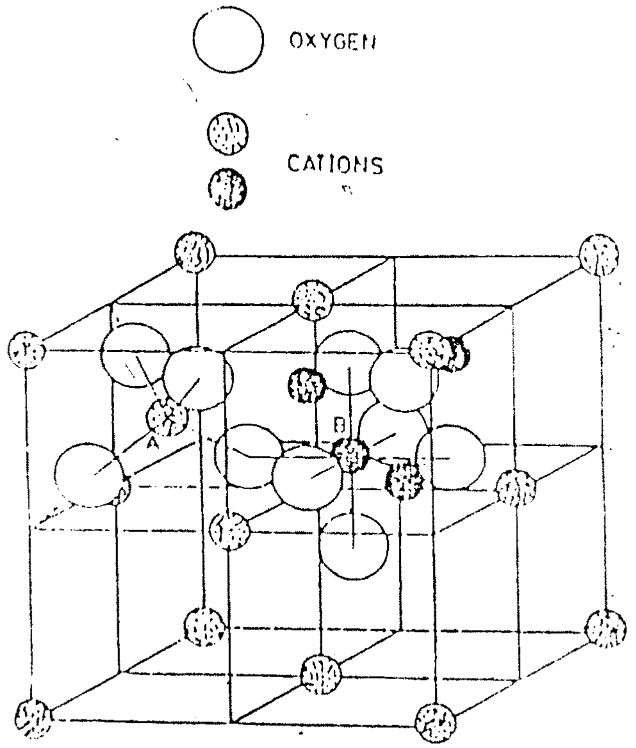

FIG. 1·1
SPINEL STRUCTURE.

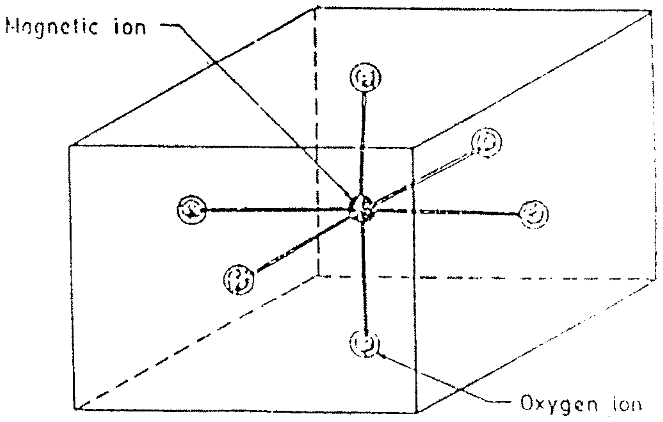

FIG. 1·2(b)
OCTAHEDRAL SITES.

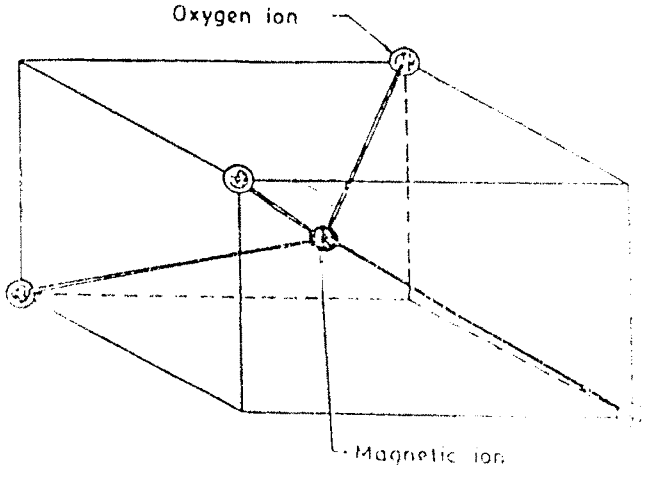

FIG. 1·2(c)
TETRAHEDRAL SITES.

The asigned space group for the cubic spinel structure is Fd3m-Oh^7. 8 cations occupy A sites and 16 cations occupy B-sites in spinel structure which are present in the unit cell. The unit cell also contains 32 anions of oxygen. The co.ordinate of ionic positions are as follows -

i) 8 A sites at 8f positions: (0,0,0) and (1/4,1/4,1/4) f.c.c.

ii)16B sites at16d positions: (5/8,5/8,5/8),(5/8,7/8,7/8),(7/8,5/8,7/8),(7/8,7/8,5/8)f.c.c.

iii) 32 positions at 32 (e) of oxygen anions are $(u,u,u),(u,\bar{u},\bar{u}),(\bar{u},\bar{u},u),(\bar{u},u,\bar{u})$,
((1/4)-u,(1/4)-u,(1/4)-u)), ((1/4)-u,(1/4)+u,(1/4)+u)), ((1/4)+u,(1/4)-u,(1/4)+u)),
((1/4)+u,(1/4)+u,(1/4)-u))

1.4 MAGNETIC PROPERTIES OF FERRITES :

In ferrites, the oxygen ion give two sub-lattice which are characterized by different oxygen environments for the metal atoms . Magnetic interaction within the sub-lattice gives rise to sub-lattice magnetisation. Magnetisation of the two sub lattice are not equal (at a temperature) and are opposite , so the net magnetisation results as a case of ferromagnetic materials . Therefore ,the ferrites exhibit all properties similar to those of ferromagnetic materials .

The properties of ferrites can be classified in to two catagories such as intrinsic and structure sensitive . saturation magnetisation , anisotropy , magnetostriction and curie temperature are the intrinsic properties ; while permeability ,hysteresis are very much structure sensitive . The structural aspects such as grain size , porosity ,impurities and inclusions of non- magnehc ions which are very much sensitive to above said properties.

Hysteresis study on ferrites gives valuable data on saturation magnetisation, coercive force , remanance ratio . Ferrites are mainly classified in different catagories based on their coercivity . coercive force can range from 0.1 Oe to 3 koe . When coercivity is 1.5 koe , the ferrites are termed as' hard ferrites '. The coercive force (Hc) of moderate or soft ferrites lie within the range from 10 Oe to 1.5 Koe. Hysteresis properties are mainly dependant on crystal structure , cation distribution, chemical composition , sintering atmosphere , heat treatment and final fabrication .

Magnetic material contains three types of domain such as multy domain (MD) , single domain (SD) and super - paramagnetic (SP) . These domain structure change with chemical composition and thermal treatment . A.C. susceptibility and Hysteresis studies are useful to explore these domain structures . The shapes of thermal variation of ac susceptibility and Hysteresis are correlated with domain strufcture . The cusp and maxima in ac susceptibility study can be correlated with anisotropy of the ferrite material. The curie temperature can also be measured when the X_{ac} is Zero at certain temperature.

The spins apart from the exchange interaction between neighbouring atoms have interaction with lattice atoms . The spin lattice interaction is seen if all the spins are completely aligned and direction of alignment is rotated relative to the crystal axes .Preferred directions of magnetic moments are then observed . The excess work done in magnetizing to saturation a specimen or ferrite in a direction , compared with the easy direction ,is called crystal anisotropy energy and it plays an important role in determining the properties like permeability , hysteresis and magnetostriction .

For cubic material , anisotropy energy is given by

$$E_A = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2)\, K_2(\alpha_1^2 \alpha_2^2 \alpha_3^2) \ldots\ldots$$

where K_1, K_2 = constants depending on material and temperature.

α_1, α_2, α_3 = Direction cosines.

Ferrites change their dimensions when they are magnetized , this is called as magnetostriction . Magnetostriction plays an important role in domain geometry and in practical use of transformer materials . The incremental change may be positive or negative depends on material at saturation . Most of ferrites exhibit negative incremental change except for few cases like Fe_3O_4.

1.5 THEORIES OF FERRIMAGNETISM :

1.5.1 Neel's Theory:

The knowledge of crystal structure and sign of magnetic interaction in it help us to account for the saturation magnetic moment and magnetic structure of a compound.

Neel [10] [11] assumed that the ferrimagnetic crystal lattice could be divided in to two sub-lattices such as tetrahedral A site and actohedral B site in a spinel structure , with fraction λ appeared on A site and fraction μ appeared on B site , so that

$$\lambda + \mu = 1 \ldots\ldots\ldots\ldots\ldots$$

He defined the interaction within the material from weiss molecular field. Neel showed that there is a antiparallel alignments of M_A and M_B for ferrmagnetism . where M_A and M_B are magnetic moments of A and B sublattices respectively .

In the presence of an applied field , Neel obtained the paramagnetic Curie temperature from the susceptibility equations .

$\chi = M/Ho$

$M = M_A + M_B$

H_O= applied field

After necessary algebric manipulation , Neel obtained the curie temperature for paramagnetic and spontaneous magnetization region as,

$$T_P = 1/2\ \gamma_{AB}\ C\ [\lambda\alpha + \mu\beta + [(\lambda\alpha - \mu\beta)^2 + 4\lambda\mu]^{1/2}]$$

for paramagnetic region and

$$T_P = 1/2\ \gamma_{AB}\ C\ [\lambda\alpha + \mu\beta - \{(\lambda\alpha - \mu\beta)^2 + 4\lambda\mu\}^{1/2}]$$

for spontaneous magnetization region Where γ is a appropriate molewlar field coefficient Tp is a curie temperature when M_A and M_B are antiparallel and Tp' is a curie temparature when M_A and M_B are parallel.

Neel further showed that the total spontaneous magnetization Msp can be written as

$M_{sp} = M_{Bsp} - M_{Asp}$

The solution of Msp with variation of temperature can not be obtained analytically and graphical method are used and known as (σ,τ) curves Fig. 1.5

where

$$\sigma = \frac{M_{sp}}{M_{sat.}}$$

Msat- saturation magnetisahon .

and $\tau = T/T_p$

The (σ ,τ) curves are p-type, m-type , R-type, N-type and V-type and depends on relative values of interactions and relative magnitudes of sub-lattice magnetisations.

1.5.2 YAFET-KITTLE THEORY:

Yafet and kittle suggested the modifications in Neel's theory as it is observed that for the spinels containing metal ions other than Fe, the magnetisation value is smaller than Neel's model. They proposed trianguler arrangement of moment by considering the possibility of subdivision of each sublattice of B site a shown in the fig. 1.6

The sub structure B1 and B2 are spontaneoussly magnetised with angle - θ other than 180° , but the resultant B is antiparallel to A. This arrangement is free from thermodynamic instabilites near 0 °k. They also proved that Neel's structure is stable if the total no. of sublattices is restricted to six , with a condition on ratio of exchange energies.

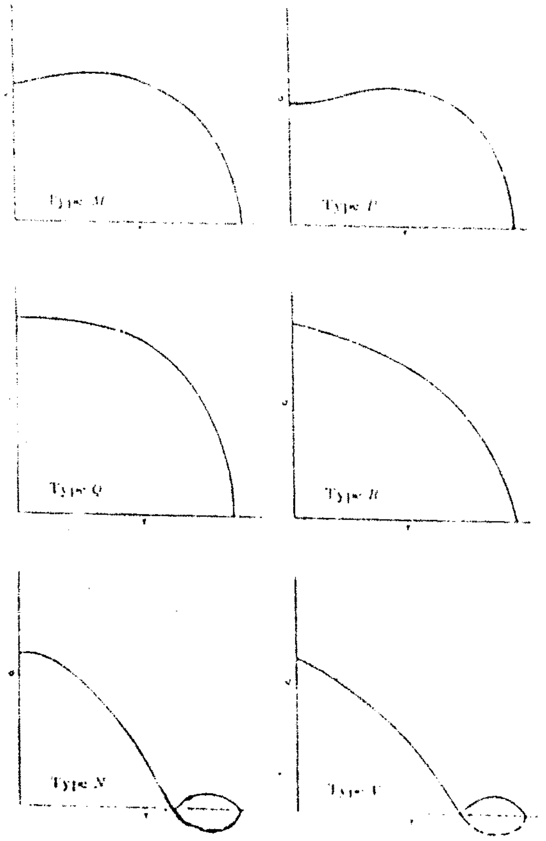

FIG. 1·5
σ-T CURVES PREDICTED BY NEEL'S THEORY.

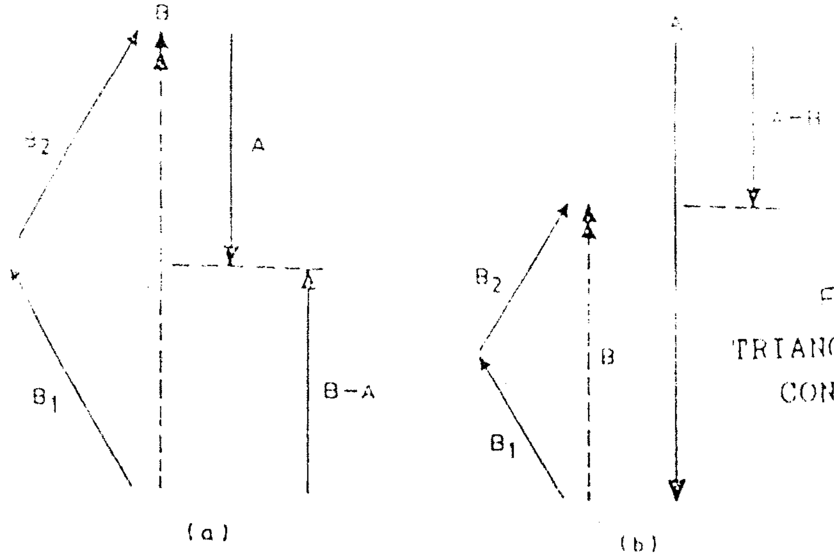

FIG. 1·6
TRIANGULAR SPIN CONFIGURATION.

1.5.3 KAPLAN'S SPIRAL STRUCTURE

Kaplan[24] proposed spiral type of spin configuration from observed Neutron diffration in some compounds .tThis structure lowers the exchange energy for the compounds he studied.

Further Lotgering [25] developed the theory of spiral configurations and applied it to experimental results.

1.6 ELECTRICAL PROPERTIES OF FERRITES:

Basically ferrites are semiconductors in nature and their resistively at room temperature vary from 10^{-3} To 10^{11} ohm cm.

The temprature dependance of resistivity obeys the law,

$$\rho = \rho_0 \,\mathrm{Exp.}(E_g / K_T)$$

Where,

E_g = activation energy

K = Boltzman constant

T = absolute temperature.

The linear relationship of log ρ versus 1/T, help to observe ferrimagnetic curie temperature [26] and to determine the activation energy [27]. The high value of activation energy [28] than 0.5 ev is associated with high resistivity at room temperature.

Ferrites show abnormally high dielectric constants and dispersion of dielectric constant in the frequency range from few Hz to few MHZ. Koops investigated the dielectric constant for Ni-Zn ferrite and describe phenomeno logical theory of dielectric behaviour (dispersion) at low frequencies . Moltgen[29] studied the Cu-Zn ferrite and Kamiyoshi [30] worked on Ni-Co ferrite, Fairweather [31] obtained the activation energy from temprature variation with relaxation time. The high dielectric constact may arise at low frequency due to the oxygen ion which have three B site and one A site neighbours . This is justfied in the view of the fact that the oxygen possesses the maximum polarizability.

Hall effect and thermoelectric properties are widely used in the interpretation of the conduction mechanism in semiconductors. Hall effect interpretation is more straight forward. However, in the case of low mobility materials such as ferrites, thermoelectrical power measurement is the only alternative. The sign of thermo emf gives vital information about the type of conduction in ferrites, whether it is p-type or n-type . Another important signifcance of thermo emf is that it enables one to calculate the values of Fermi energy and carrier concentration [32] .

1.7 ORIENTATION OF PROBLEM :

Ferrites continue to evoke interest because they are the most improtant electronic and magnetic ceramics. The simultaneous twin requirement of optimal electronic and magnetic properties in the advanced electronics, microwave and computer technologies have focused the attention of research workers of ferrites Hence, ferrites which are ferrimagnetic semiconductors opened a new vista in the physics of materials and need for high resistively ferrites led to the synthesis of various ferrites. The increasing demand for low loss ferrites resulted in detailed investigations on the various aspects of coductivity and on the influence of various substitutions on the electrical conductivity, thermoelectric power, Hall mobility etc.

Mg ferrite is technologically important ferrite because of its high resistivity. Therfore, the combination of various diavalent cation like Mn ,Zn ,Cu, etc are used to increase the losses.

New methods of prepration have improved the ferrites properties ties . To obtain high density and chemical homoginity, the chemical route methods are useful. Therfore in order to understand the role of co-pre cipitation method of ferrite preperation on physical properties, the following work will be undetaken during this course period .

1.Preparation of Mg- Zn , Cu-Zn, Mg -Cu ferrites by chemical method , Zn concentration is optimised to achieve the higher value of magnitisaton as well as curie temprature of about 250 to 300°c.

2. x-ray diffraction and I. r. studies .

– to confirm the single phase fromation

– to determine the crystal structure and lattice constant.

–internal variation of feerrite

3. Electrical propeties

a) D.C conductivity

b) Thermo emf

4. Magnetic studies

To determine the cation distribution

5. A.C. susccptibility.

To observe the domain structure.

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