

# Magnetization and Magnetic Behavior of $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ Ferrites

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## ABSTRACT

This article describes the experimental investigation on the magnetization behavior of  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ferrites for  $x \geq 0.0$  &  $\leq 0.8$  prepared by conventional ceramic method. Magnetic properties have been measured as a function of field and temperature using vibrating sample magnetometer and SQUID magnetometer. Saturation magnetization at 20 K increases with Cd-content up to  $x = 0.5$  and decreases thereafter. Neel's two sublattice collinear model is applied for the initial rise of the magnetization up to  $x \leq 0.5$  and beyond that three sublattices non-collinear model proposed by Yafet-Kittel are predominant. This indicates the appearance of spin canting structure in  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ferrites with higher Cd-content. Sample with  $x = 0.8$  shows anomalous temperature dependent magnetic ordering on applied magnetic field. Low field (5 Oe) magnetization shows antiferromagnetic ordering while the ferromagnetic ordering has been found to be dominant with the high field (1 T). That is the magnetic ordering of  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  is dependent on the strength of applied field.

**Keywords:** Saturation magnetization, spin canting, magnetic ordering, ferromagnetic ordering, antiferromagnetic ordering.

## 1. INTRODUCTION

Ferrites have proved them commercially important magnetic materials ranging from the very ordinary radio sets to the complicated and exhaustive hardware involved in computers. Ferrites are extensively used in many kinds of magnetic devices such as transformers, inductors, magnetic heads, in resonance circuits for high frequency (ranging from  $10^3$  to  $10^{11}$ Hz) because of their high electrical resistivity, low eddy current losses, high initial permeability, high saturation induction, low hysteresis loss and reduced physical size. For these reasons, extensive research work has been continued over the past few decades to improve their qualities and efficiencies from the application point of view to various technical devices.

In this work soft ferrites with cubic spinel structure with a composition of  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ferrites for  $x = 0.00$  to  $0.80$  in steps of  $0.10$  have been carried out. Spinel ferrites are derived from magnetite,  $\text{Fe}_3\text{O}_4$  by partial substitution of the iron ions by other cations. The general chemical formula spinel materials is  $\text{AFe}^{3+}_2\text{B}_x\text{O}_4$ , where A represents a divalent cation, or a combination of cations with an average valency of two, and B is a trivalent cation or a combination of cations with an average valency of three. The composition parameter can range between zero and two, but it is obvious that if  $x$  is close to two, these oxides cannot be considered as ferrites anymore.

Although the spinel ferrite materials are widely used for so many years in eletro-technical equipment,

much research and development in this field is still in progress, from the basic as well as from the application point of view. Although there have been no novel developments in ferrite materials and components, world production of ferrites is still increasing and the development problems connected with these technically important materials are yet to be solved. As magnetic materials, ferrites are still the best in high frequency and very high frequency circuits and they cannot be replaced by other magnetic elements, since they are relatively inexpensive and easy to fabricate [1]. A wide variety of information regarding the development and study of electromagnetic, dielectric and optical properties are available in Refs. [2-4].

In cubic spinel ferrite there are two sub-lattices: tetrahedral (A-site) and octahedral (B-site). Structural, electro-magnetic and other properties of spinel ferrites responsible for their applications have been reported to be strongly dependent upon the cationic distributions on these sites [5]. Therefore, there are enormous opportunities to carry out research in order to improve their magnetic and other qualities by various cationic replacements in A-site or B-site [6]. In spinel ferrites cations are found to residing on the tetrahedral A-sites and octahedral B-sites. Due to the existence of these cations inter-sublattice ( $J_{AB}$ ) and intra-sublattice ( $J_{AA}$ ,  $J_{BB}$ ) exchange interactions have been found to occur. It is generally believed that the magnetic properties of spinel ferrites depend upon the relative strengths of these types of exchange interactions. When the cations of A and B sites are totally magnetic, the inter-exchange interactions  $J_{AB}$  are much stronger than  $J_{AA}$  and  $J_{BB}$  interactions i.e.,  $|J_{AB}| \gg |J_{BB}| \gg |J_{AA}|$ . On that occasion, spins have a collinear structure in which moments on the A-sites are anti-parallel to the moments on the B-sites. However, when one of the intra-sublattice interactions

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becomes comparable with the inter-sublattice interaction it leads to a non-collinear spin structure [7].

With the addition of nonmagnetic  $\text{Cd}^{2+}$ , magnetic dilution occurs. Due to magnetic dilution, frustration/disorder of certain moments should occur leading to collapse of the co-linearity of the ferrimagnetic phase and the effective moments are created within the ferrimagnetic structure by local canting around the magnetic imperfections. In addition to that sufficiently diluted ferrites with non-magnetic ions can show a wide spectrum of magnetic order ranging from ferrimagnetism, anti-ferromagnetism, local canted spin to semi-spin glass, spin glass, cluster spin-glass properties and paramagnetic behavior.  $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ferrites are widely used in various electromagnetic devices due to their high resistivity, high permeability, and comparatively low magnetic losses. Nickel ferrites are partially inverse spinel while cadmium and zinc ferrites are normal spinel. Both  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions are non-magnetic and prefer to occupy the tetrahedral sites only [4]. Therefore it would be interesting to substitute Cd with Ni to understand its effect on the magnetization and magnetic behavior, which are hitherto not been studied in much detail. Since, the ionic radius of Cd is larger than Zn, the substitution of Cd with Ni would give rise to new magnetic interactions which in turn might significantly modify the and magnetization behavior of Ni-Cd ferrites.

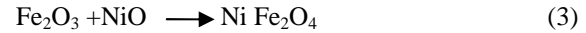
## 2. EXPERIMENTAL DETAILS

Generally, preparation technique of polycrystalline ferrites consists of four major steps: preparing a mixture of materials with the cations more or less in the ratio corresponding to that in the final product, prefiring the mixture, conversion the 'raw' ferrite into powder and pressing the powder into the required shapes, and sintering. The raw materials used are oxides of iron, nickel oxide and cadmium oxide. The high purity of raw materials of analytical research grade was used as supplied by the manufacturer E. Mark of Germany. The constituents in required stoichiometric proportions were weighed first and then were thoroughly mixed using ceramic mortar and pestle. The resultant powders were then ball milled for 6 to 8 hours to produce fine powders of mixed constituents. To avoid iron contamination, mixing was done with stainless steel balls in a steel ball milling machine and a fluid such as distilled water is used to prepare the mixture into slurry.

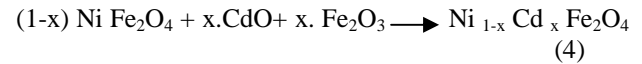
The slurry was transferred to a porcelain crucible for prefiring. Prefiring was done at a constant temperature of 1200 °C. More details about the formation on Ni-Cd ferrites preparation by conventional mixed oxides ceramic methods are available in Refs. [1-8]. During the prefiring stage, the reaction of  $\text{Fe}_2\text{O}_3$  with metal oxide (say MO or  $\text{M}_2\text{O}_3$ ) takes place in the solid state to form spinel according to the reactions:



The NiO creep into  $\text{Fe}_2\text{O}_3$  to form an intermediate phase  $\text{NiFe}_2\text{O}_3$  at low temperature in the following manner:



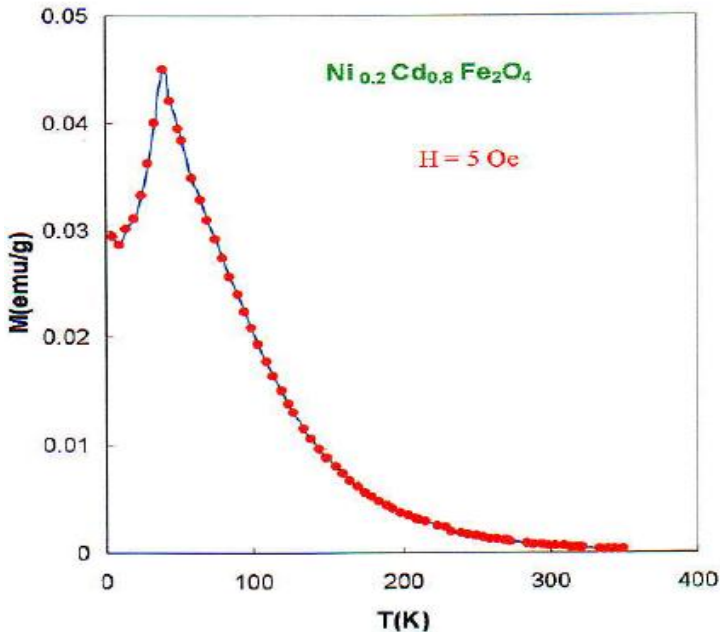
After that Cd ions are introduced by



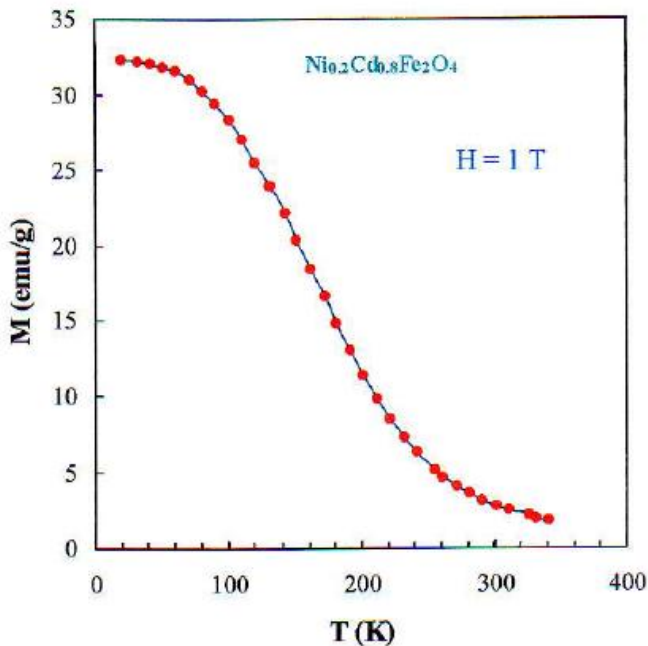
Polyvinyl alcohol was added as a binder to the ground homogeneous powder. Pressing the powder into compacts of desired shapes was done by conventional method in a die-punch assembly. Cylindrical and toroidal shaped samples were made by this process. A uniform pressure of 60 bar has been maintained throughout the process. At the final stage preparation of ferrite products sintering has been done at a temperature of 1250<sup>0</sup> C for 8 hours in air to fulfill the following requirements: to bond the particles together so as to impart sufficient strength to the products, to densify the green compacts by eliminating the pores and to homogenize the materials by completing the reactions left unfinished in the presintering stage. Details about the sample preparation technique and various properties of these types of materials are available elsewhere [9-12].

## 3. RESULTS AND DISCUSSION

Fig. 1 and 2 show the temperature dependence of magnetization of Ni-Cd ferrites at low field (5 Oe) and high field (1 T) respectively. This is noteworthy that Ni-Cd ferrites show interesting magnetic ordering with temperature as dependent on applied magnetic field. According to the magnetization curve shown in Fig. 1 with  $H = 5$  Oe, it is observed that the sample does not show any sign of ferromagnetism; rather it demonstrates a feature of antiferromagnetic ordering. From Fig. 1, it is noticed that as the temperature decreases,  $M$  increases in a manner as manifested in a paramagnetic substance, passing through a maximum at a critical temperature of 39 K and falls thereafter. This critical temperature of 39 K for  $x = 0.8$  may be termed as antiferromagnetic transition temperature,  $T_N$ . Above  $T_N$ , the sample behaves as a paramagnetic substance and below  $T_N$  as an antiferromagnetic material. However, at high field  $H = 10000$  Oe (1 T), a different scenario has been observed with the absence of maxima (peak) and the nature of the temperature dependence of magnetization resembles ferromagnetic nature. The ferromagnetic transition temperature,  $T_c$  is difficult to extract from this high field magnetization curve due to the smearing of inflexion point by high field effect. This type of magnetic behavior with temperature with high content of non-magnetic cations such as Zn and Cd is generally observed in Ni, Li and Mg based ferrites [13]. It is known that  $\text{CdFe}_2\text{O}_4$  and  $\text{ZnFe}_2\text{O}_4$  are paramagnetic at room temperature and show antiferromagnetic



**Fig 1:** Temperature dependence of magnetization of  $\text{Ni}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  at low field (5 Oe).



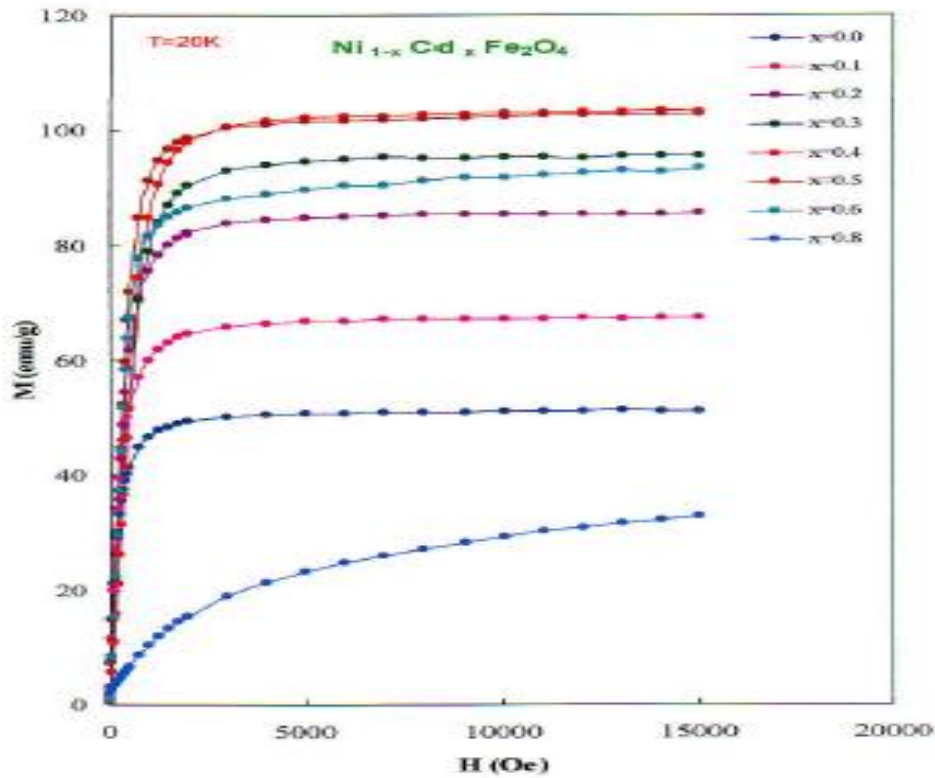
**Fig 2:** Temperature dependence of magnetization of  $\text{Ni}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  at high field (1 T).

behavior at very low temperature [15]. When these ferrites are substantially diluted with higher content of non-magnetic  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , spin canting and spin frustration takes place giving rise to antiferromagnetic/anomalous behavior as a function of temperature.

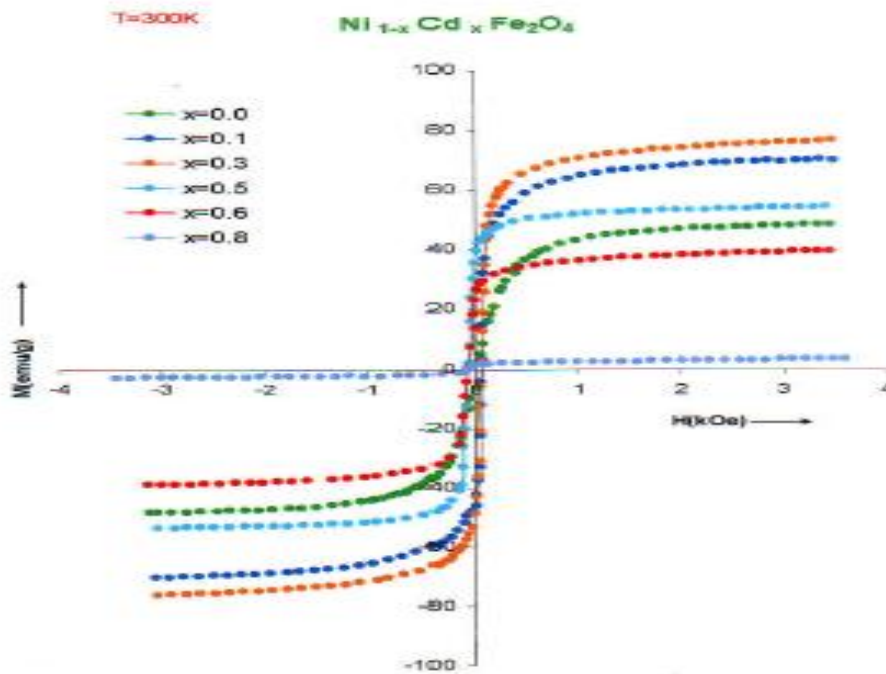
According to the Neel's model, the magnetic ordering in the simple spinel ferrites is based on the Neel's two sub-lattices (A-sites and o B-sites) and the resultant magnetization is the difference between A-site and B-site magnetization, provided that they are co-linear and anti-parallel to each other. Mathematically,

$$M = M_B - M_A \quad (5)$$

Fig. 3 show the magnetization of Ni-Cd ferrites as a function of field at different amount of cadmium content at 20 K measured with a SQUID magnetometer while Fig. 4 shows the same measured with a VSM at room temperature. The magnetization of all the samples are saturated except for  $x = 0.8$ . The sample with  $x = 0.8$  shows monotonous increase of magnetization with increasing magnetic field with no sign of saturation. Saturation magnetization increases with the increase of Cd-content initially and then decreases thereafter. Sample with  $x = 0.8$  shows paramagnetic behavior at room temperature. The saturation magnetization of a sample has been taken at high field where  $M$  is independent of magnetic field. The results of the saturation magnetization,  $M_s$ , at room temperature and at 20 K are shown in Table 1 [15]. Fig. 5 shows the effect of Cd-content on the  $M_s$  of the  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ferrites measured at 20K and room temperature. It is observed that magnetization increases with Cd-content up to  $x = 0.3$  at room temperature and up to  $x = 0.5$  at 20K. Above these concentration magnetization decreases sharply. The initial increase of magnetization is due to the dilution of magnetic moment of A-sublattice by substitution of nonmagnetic Cd-ions. Since the resultant magnetization is the difference between the B and A sublattice magnetization as shown in Eq. 5, it is obvious that increase of net magnetization is expected on dilution of the A-sublattice magnetization due to occupation of A-site by nonmagnetic Cd-ions as well as enhancement of B-sublattice magnetization due to the introduction of  $\text{Fe}^{3+}$  ions having  $5 \mu_B$  moment. This initial rise of magnetization can be explained on the basis of Neel's two sublattice model.



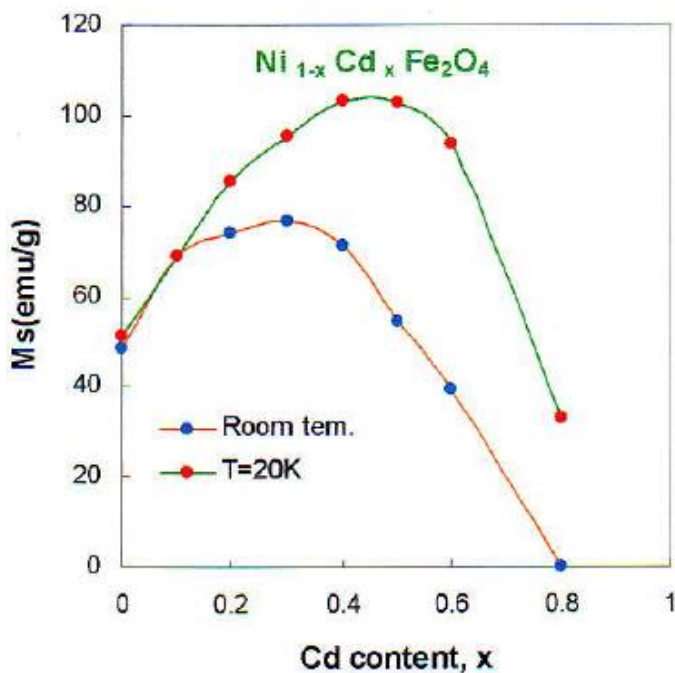
**Fig 3:** Magnetization of  $\text{Ni}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  ferrites as a function of field at different Cd-content at 20K (SQUID measurements data).



**Fig 4:** Magnetization of  $\text{Ni}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  as a function of field at 300 K sintered at  $1200^\circ\text{C}$  in air for 4 hours (VSM measurements data).

<http://www.ejournalofscience.org>**Table 1:** Saturation magnetizations of  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  ferrites [15].

Cadmium content x	Saturation magnetization at room temperature, $M_s$ (emu/g)	Saturation magnetization at 20K $M_s$ (emu/g)
0.0	48.4	51.2
0.1	69.1	69.1
0.2	73.7	85.5
0.3	76.5	95.5
0.4	71.2	103.2
0.5	54.4	102.7
0.6	39.3	93.4
0.8	0.0	32.8

**Fig 5:** Saturation magnetization of  $\text{Ni}_{0.2}\text{Cd}_{0.8}\text{Fe}_2\text{O}_4$  as a function of Cd-content at room temperature and at 20K (SQUID measurements data).

The decrease of magnetization beyond  $x = 0.3$  at room temperature and  $x = 0.5$  at 20 K is that beyond this limit the magnetization of A-sublattice is so much diluted that the A-B exchange interaction becomes weaker or comparable with the B-B exchange interactions. This disturbs the parallel arrangement of spin magnetic moments on B-site paving way for canted spins.  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  substituted ferrites have the tendency of manifestation of similar type of canting behavior above a certain limit of their contents [16-17]. The existence of canted spin gives rise to Yafet-Kittel (Y-K) angle which compares the strength of A-B and B-B exchange interaction. Neel's two sublattice model is unable to explain the decrease of magnetization. The decrease of magnetization can be treated theoretically by triangular arrangement of spins as proposed by Yafet and Kittel according to Ref. [18]. The Y-K angles are found to increase with the increase of Cd-content [19]. The physical origin of this spin arrangement is from the canting of the spins in the B-sublattice due to weakening of the intersublattice interaction  $J_{AB}$  and enhancing of intersublattice interaction  $J_{BB}$  on nonmagnetic Cd-substitution in the A-sublattice. As in the case of spinels,  $J_{BB}$  is antiferromagnetic, the B-sublattice splits into two sublattices forming YK angle between the directions of the spins resulting in a decrease of net B-sublattice magnetization. Neutron diffraction study on Ni-Zn ferrites with high content of Zn have reported the occurrence noncollinear spin arrangements which in turn results in a sharp decrease of magnetization [20]. If the spin canting has not occurred with higher Cd-content, the magnetic moment of the entire series would increase monotonically reaching a value of  $10 \mu_B$  for  $\text{CdFe}_2\text{O}_4$  [15].

#### 4. CONCLUSIONS

It is well known that both Zn and Cd are paramagnetic. The ionic radius of  $\text{Cd}^{2+}$  ( $0.97 \text{ \AA}$ ) is larger than that of  $\text{Zn}^{2+}$  ( $0.83 \text{ \AA}$ ). Hence, it is believed that substitution of Cd in  $\text{Ni}_{1-x}\text{Cd}_x\text{Fe}_2\text{O}_4$  may show some interesting properties since  $\text{Cd}^{2+}$  with larger ionic radius causes some lattice distortions. Replacement of smaller  $\text{Fe}^{3+}$  ions ( $0.64 \text{ \AA}$ ) from A-sites to B-sites by larger  $\text{Cd}^{2+}$  ( $0.97 \text{ \AA}$ ) might cause new types of magnetic interaction which in turn results in the modification of the magnetization behavior of Ni-Cd ferrites. Magnetization of Ni-Cd ferrites have been measured as a function of temperature, field, and composition using vibrating sample magnetometer and SQUID magnetometer. Magnetizations of Ni-Cd ferrites measured with a SQUID magnetometer as a function of field at 20K has been found to be consistent that measured with a VSM at room temperature. Magnetization of all the samples have been found to be saturated except for  $x = 0.8$ . Sample with  $x = 0.8$  shows monotonous increase of magnetization with increase in magnetic field with no sign of saturation. Saturated magnetization increases with the increase of Cd-content initially and decreases thereafter. Composition with  $x = 0.8$  shows paramagnetic behavior at room temperature. Saturation magnetization increases with Cd-content up to  $x = 0.3$  at room

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temperature and up to  $x = 0.5$  at 20 K. Above these concentration magnetization decreases sharply. Initial increase of magnetization is due to the dilution of magnetic moment of A-sublattice by substitution of nonmagnetic Cd-ions. Neel's two sublattice collinear model is applied for the initial rise of the magnetization up to  $x \leq 0.5$ , at 20K and beyond that three sublattice noncollinear model proposed by Yafet-Kittel are predominant. This suggests the existence of canted spin structure in Ni-Cd ferrites with higher Cd-concentration.

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