

A study of ultrasonic velocity and attenuation on polycrystalline Ni–Zn ferrites

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Abstract. Polycrystalline NiZn ferrites with different grain sizes (1.2 μm to 10.2 μm) were prepared by the usual ceramic method. The magnetic properties were measured at room temperature. The ultrasonic velocity and attenuation were measured on Ni–Zn ferrite by using the pulse transmission method at 1 MHz, in the temperature range 300–600 K. The velocity was found to be slightly sample dependent at room temperature and decreased with increasing temperature, except near the Curie temperature, T_c , where a small anomaly was observed. The longitudinal attenuation (a_l) at room temperature was found to be more sample dependent. The temperature variation of ultrasonic longitudinal attenuation exhibited a broad maximum around 400 K and a sharp maximum just below Curie temperature (T_c). The above observations were carried out in the demagnetized state. The application of a 380 mT magnetic field allowed us to reach the saturated state of the sample at all the measuring temperatures. The anomaly observed in the thermal variation of velocities (longitudinal and transverse) and attenuation has been qualitatively explained with the help of the temperature variation of the magneto-crystalline anisotropy constant.

Keywords. Ferrites; magnetic properties; ultrasonic velocity; attenuation; domain walls.

1. Introduction

There is an abundant literature on the propagation of ultrasonic waves in magnetic materials, but a few interpretations only refer to possible effects due to the domain wall (DW) (Le Craw *et al* 1960). It was known from the acoustic emission (AE) studies on magnetic materials that the space occupied by a DW is the location of magneto-elastic interactions and ultrasonic bursts are emitted when the DW are created or annihilated (Guyot *et al* 1989; Guyot and Cagan 1991). It was also found that the specific DW/lattice magneto-elastic interactions might be one of the origins of the DW relaxation. In order to understand interaction of DW with ultrasonic velocity, a detailed study of the thermal variation of ultrasonic longitudinal (V_l) velocity, transverse (V_s) velocity and longitudinal attenuation (a_l) on a series of polycrystalline Ni–Zn ferrites was undertaken and the results thus obtained are presented here.

2. Experimental

High purity polycrystalline samples were prepared by using a ceramic method (Murthy 1979). Pure (99.99%) NiO, ZnO and Fe₂O₃ powders with different particle sizes were used for the preparation. α -Fe₂O₃ coarse particles (average diameter 0.13 μm) were synthesized by oxidation of Fe₃O₄ particles at 800°C. Industrial grade particles

of Ni and Zn oxides were used as the coarse particles with average diameters of 0.6 μm and 0.16 μm , respectively. Fine particles of Ni and Zn oxides were synthesized by thermal decomposition of Ni and Zn oxalate at 400°C in air. These powders were mixed together with wet attrition milling. Their molar ratio was adjusted to Ni_{0.46}Zn_{0.54}Fe₂O₄. All the dried powders were calcined at 800°C for 6 h in air and re-ground by wet ball milling for 100 h to form slurry. Then the powder was passed through a sieve (60 mesh). To this powder, 2 wt% poly-vinyl-alcohol was added as a binder. The granules were compacted at a pressure of 190 MPa for 10 min, into plates, rods and toroidal shaped samples. By selecting the proper combination of time of grinding and compacting pressure, the porosity and grain diameter of the samples were varied independently (Globus 1977). The specimens were heated up to 400°C to remove the binder and the lubricant. Finally, the samples were sintered at 1000°C/50 h, 1050°C/50 h, 1100°C/50 h, 1150°C/100 h and 1250°C/100 h in air. The rate of heating and cooling during the sintering was 20°C/h.

The mono-phasic nature of the samples was studied with the help of X-ray analysis. Sintered density was determined by measuring the dimensions and weight. Each specimen was ground, polished by the standard metallurgical procedure, and then etched thermally at a temperature of 100–150°C for 30 min. The etched sample was examined using optical microscopy. Average grain size (D_m) was measured using the relation:

$$D_m = S/x^2 - N,$$

where S is the surface of the photographed part of the sample, x the linear magnification, and N the number of grains in the surface S . The room temperature magnetic properties were obtained by recording hysteresis loops with the help of vibrating sample magnetometer (VSM).

A conventional ultrasonic pulse transmission technique was used to measure the velocities and attenuation at 1 MHz (Papaiah 1992). The samples were inserted into a controlled temperature chamber which in turn were placed in between the pole gap of an electromagnet. This allowed us to measure the field and temperature dependence of the ultrasonic velocities and attenuation. The magnetic field was always applied parallel to the length of sample. The accuracy in the velocity and attenuation measurements is 0.01% and 0.5%, respectively.

3. Results and discussion

It can be seen from table 1 that the sintered density reached 98.8% of the theoretical density at 1050°C. The ultra fine particle size and relatively uniform grains are believed to be responsible for achieving this very high densification at low temperature, compared to much higher temperatures normally employed with the conventional process (~ 1300°C). We could not reach the theoretical value because, the ferrite particle being too fine to be completely dispersed in the liquid suspension and, therefore, flocculated to some extent by Van der Waals bonding. This slightly flocculated suspension resulted in some agglomerated regions distributed in the microstructure of samples. This was confirmed by microstructure. Rearrangement and differential microdensification processes could not, thus, be wholly avoided during the sintering of these slightly inhomogeneous packed compacts and therefore completely dense fired bodies were not achieved.

The microstructure of sintered specimens indicated relatively uniform grains with the porosity situated solely at the grain boundaries. The use of fine ferrite powders may be responsible for the intergranular porosity. It can be seen from table 1 that simultaneous grain growth and densification occurs in the present samples. At 1100°C the compact densified readily up to 99% of the theoretical maximum and grain size increased to about 5.8 µm. At

temperatures > 1150°C, significant grain coarsening occurred with the grain size increasing from 6.9 to 10.2 µm at 1250°C.

In the present experiment, the Ni-Zn ferrites have densities in the range 5.29–5.32 g/cm³. This density variation is small compared to the variation of grain size (1.2–10.2 µm). Therefore, grain size, not density, has the dominant effect on various properties. The average value of lattice constant in the present samples is 8.416 Å which is in good agreement with the literature value (Agajanian and Turk 1966; Murthy 1979).

Magnetic properties such as saturation magnetization (M_s), remanence (M_r) and coercivity (H_c) obtained from the recorded hysteresis loops are presented in table 1. As the sintered density is same for present samples, the values of M_s and M_r are also found to be nearly same. However, H_c is highly independent of the density, but dependent on the grain size of the samples and varies with the reciprocal of grain size. Globus (1977) studied the relationship between the hysteresis loop and the grain size for YIG. The experimental results show that the coercivity is inversely proportional to the average grain size, and that the remanence is independent of the grain size. Igarashi and Kazaki (1977) also indicated, through experiments and theoretical derivation, that H is inversely proportional to grain size, D_m . Similar result was also observed by many others in the case of Ni-Zn and Mn-Zn ferrites (Stopples 1980; Pyun and Baek 1985).

Table 2 gives the room temperature values of longitudinal (V_l) and transverse (V_s) velocities along with the computed values of elastic constants; Young's (Y), shear (m), and bulk modulus (K). The room temperature values of α_1 are also included in table 2.

It is clear from the table that the room temperature velocities V_l and V_s increased from 6.24 km/s to 7.56 km/s and 3.38 km/s to 3.89 km/s, respectively with an increase in density. Reciprocally, the attenuation coefficient was found to decrease from 0.58 to 0.2 dB/cm. In the present samples the increase in density has increased the grain size from 1.2 µm to 10.2 µm. As the porosity of samples remained constant, the increase in the velocities and decrease in the attenuation may be considered due to an increase in the grain size. It can be seen from the table that the values of Y and μ are also found to increase with an increase of grain size. These observations are in good agreement with results of

Table 1. Magnetic properties of Ni-Zn ferrites at room temperature.

Sample no.	T_s (C/h)	% Theor. density	Grain size (µm)	B_s (mT)	H_c (A/m)	M_r (Am ⁻² /kg)	μ_i (1 MHz)
NZ-1	1000/50	98.3	1.2	340	33	45	49.65
NZ-2	1050/50	98.8	4.5	345	24	48	73.15
NZ-3	1100/50	99.0	5.8	348	22	45	128.55
NZ-4	1150/100	99.0	6.9	350	21	45	225.12
NZ-5	1250/100	99.0	10.2	350	20	46	285.34

Papadakis (1965). The value of Poisson's ratio (s), however, remains constant ($= 0.31$) within the experimental error.

Young's modulus for Ni-Zn ferrite of composition $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ has been determined by Weil *et al* (1951) using the resonant frequency of radial oscillations in a ring. For a specimen of density $4.5 \times 10^4 \text{ kg/m}^3$, the value of Y is given as $11.7 \times 10^{10} \text{ N/m}^2$. Van der Burgt (1953) measured the dynamic elastic constants for the Ni-Zn ferrites by using the magnetostrictive method of excitation. He measured the Y and μ on the toroids and tubular samples of diameters $\sim 2 \text{ mm}$ and 4 mm . The values of Y and μ for different compositions obtained by him are $18.9 \times 10^{10} \text{ N/m}^2$ and $7.1 \times 10^{10} \text{ N/m}^2$ for $\text{Ni}_{0.3}\text{Zn}_{0.7}\text{Fe}_2\text{O}_4$; $18.4 \times 10^{10} \text{ N/m}^2$ and $6.9 \times 10^{10} \text{ N/m}^2$ for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$; and $18.1 \times 10^{10} \text{ N/m}^2$ and $6.6 \times 10^{10} \text{ N/m}^2$ for $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$, respectively. Revathi and Rao (1973) measured the elastic constants of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($X = 0, 0.3, 0.5, 0.3$ and 0.1) by using the composite piezo-electric oscillator method. The values of Y and μ obtained by them are $17.73 \times 10^{10} \text{ N/m}^2$ and $7.17 \times 10^{10} \text{ N/m}^2$ when $X = 0$, $17.44 \times 10^{10} \text{ N/m}^2$ and $6.33 \times 10^{10} \text{ N/m}^2$ when $X = 0.3$, $17.25 \times 10^{10} \text{ N/m}^2$ and $6.14 \times 10^{10} \text{ N/m}^2$ when $X = 0.5$, and $16.84 \times 10^{10} \text{ N/m}^2$ and $5.94 \times 10^{10} \text{ N/m}^2$ when $X = 0.7$, respectively. Murthy

et al (1978, 1981) measured the values of Y and μ for Ni-Zn ferrites by using the composite oscillator method. The values of Y and μ obtained by them for the sample with composition $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ are $17.42 \times 10^{10} \text{ N/m}^2$ and $6.29 \times 10^{10} \text{ N/m}^2$. We in this study obtained value of Y for the polycrystalline Ni-Zn samples which varied from $15.51 \times 10^{10} \text{ N/m}^2$ to $21.12 \times 10^{10} \text{ N/m}^2$. Similarly, the value of μ varied from $6.01 \times 10^{10} \text{ N/m}^2$ to $8.01 \times 10^{10} \text{ N/m}^2$ (table 1). Thus, our values are in fair agreement with that of the reported values, when the values are compared for specimens of the same or nearly the same density and composition.

Figures 1 and 2 give the thermal variation of the longitudinal and transverse velocities measured in the demagnetized state for all samples. It can be seen from the figures that the values of V_L and V_S decreases smoothly with increasing temperature and attain a minimum at a certain temperature (T_1) below the Curie point. Beyond this temperature the velocities show a positive temperature coefficient and attain a maximum value at a temperature T_2 . With further increase of temperature both the velocities are found to decrease. It is also observed that the longitudinal velocities measured on the samples NZ-4 and NZ-5 are very close to each other and their variation

Table 2. Room temperature preparation and elastic modulus data for Ni-Zn ferrites.

Sample no.	V_L (m/s)	V_S (m/s)	a_1 (dB/cm)	$Y \times 10^{-10}$ (N/m ²)	$\mu \times 10^{-10}$ (N/m ²)	$K \times 10^{-10}$ (N/m ²)	s
NZ-1	6250	3381	0.58	15.51	6.01	12.30	0.31
NZ-2	6482	3668	0.55	18.06	7.17	12.54	0.31
NZ-3	6532	3571	0.43	18.80	7.52	12.53	0.31
NZ-4	7471	3807	0.33	20.09	7.52	19.70	0.31
NZ-5	7558	3892	0.31	21.12	8.00	19.56	0.31

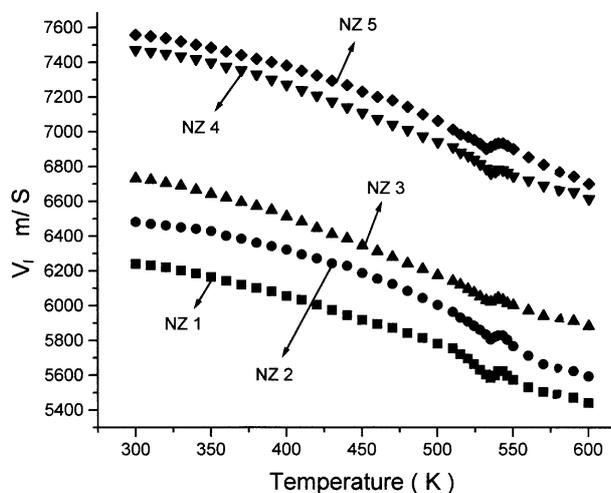


Figure 1. Thermal variation of longitudinal velocity (V_L) for Ni-Zn ferrites.

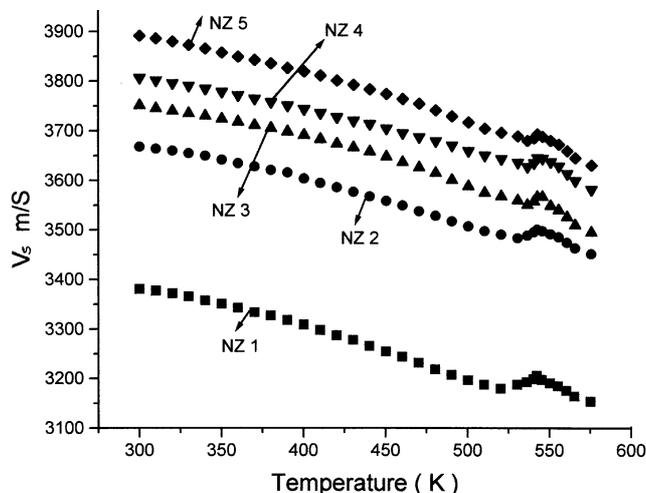


Figure 2. Thermal variation of shear velocity (V_S) for Ni-Zn ferrites.

is about 8.8% between 300 K and T_c . For samples, NZ-1, NZ-2 and NZ-3, the values of V_1 are found to decrease by about 10% between 300 K and T_c . In all these samples anomalous behaviour occurs in between 525 K and 540 K. The thermal variation of V_S for all the samples is found to be similar and the variation is about 5% between 300 K and T_c . A less (535 to 540 K) pronounced increase of V_S with temperature is observed near the Curie point. No hysteresis has been observed during cooling.

At a given temperature velocity decreases when the mean grain size increases; this tendency is maintained all over the investigated temperature range. The decrease of V_1 and V_S with temperature is mainly due to the softening of the material.

Murthy and Rao (1979, 1983) have observed a similar anomalous behaviour in the thermal variation of longitudinal and shear velocities for Ni-Zn, Co-Zn and Mn-Zn ferrites in the vicinity of the Curie temperature. Novikov and Stel'mashenke (1967) and Kawai and Ogawa (1978) in the cases of NiCaMn and Mn ferrites also have observed, respectively a similar anomalous variation of Young's modulus near the Curie temperature.

The anomalous behaviour of ferrites can be explained qualitatively with help of the temperature variation of the magneto-crystalline anisotropy constant (k_1). The temperature variation of k_1 was measured on the brother samples and found that k_1 becomes zero just below the Curie temperature i.e. at 523 K (Papaiah 1992). The measurements of initial permeability vs temperature on the brother sample, has shown that the Curie temperature of the present samples is 538 K.

As can be seen from figures 1 and 2, the V_1 and V_S for present samples have reached a minimum value at temperature 525 K (T_1), while k_1 becomes zero at 523 K. Similarly, the V_1 and V_S attain a maximum value at a temperature 540 K (T_2), while the Curie point of samples

under investigation is 538 K. Thus, the minimum (T_1) and maximum (T_2) temperatures of V_1 and V_S vs temperature plots coincides with temperatures of $k_1 = 0$ and the Curie temperature, respectively.

The magneto-crystalline anisotropy constant can be considered as a measure of the magnetic energy barrier to the movement of domain walls in the magnetic materials. As such, domains will be free to move at a temperature at which $k_1 = 0$, the substance undergoes a maximum strain for a given stress, in other words the V_1 and V_S increases till the Curie temperature is reached. Beyond the Curie temperature, both the velocities show a decrease with an increase of temperature, since at T_c the ferrite loses its spontaneous magnetization and becomes paramagnetic.

In figures 3 and 4, for the sample NZ-1, we present the temperature dependence of V_1 and V_S measured both in $H = 0$ and with $H = 380$ mT; this field was found to be high enough to saturate the sample at any of the measuring temperatures. In saturated state V_1 (or V_S) is slightly higher than in the demagnetized state, except above T_c , where both the values are identical, as expected. When the sample is subjected to magnetic field, it is observed that the minimum of velocity-temperature curve is shifted to the low temperature side and becomes shallow. As the magnetic field increased further the minimum continued to shift to the low temperature side becoming more and more shallow. Finally the dip disappeared when the magnetic field was equal to saturation field of the sample. This was because at the saturation value the domain wall movement was frozen completely.

The magnetic contribution to the velocity variations with temperature can be considered as a 'second order effect', superimposed on the purely mechanical effects; it is more pronounced for the large grain size samples. The magnetic contribution dV_1 or dV_S defined as the difference between the velocity in the saturated and demagnetized states is, respectively given by: $dV_1 = V_1(H = 380 \text{ mT})$

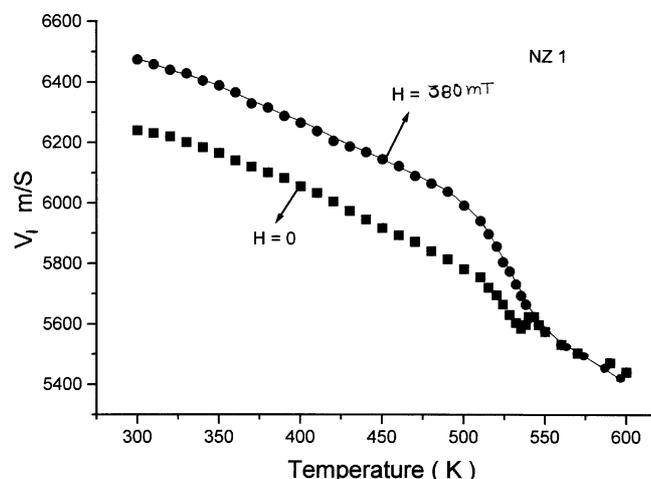


Figure 3. Thermal and magnetic field variations of V_1 for NZ-1 ferrites.

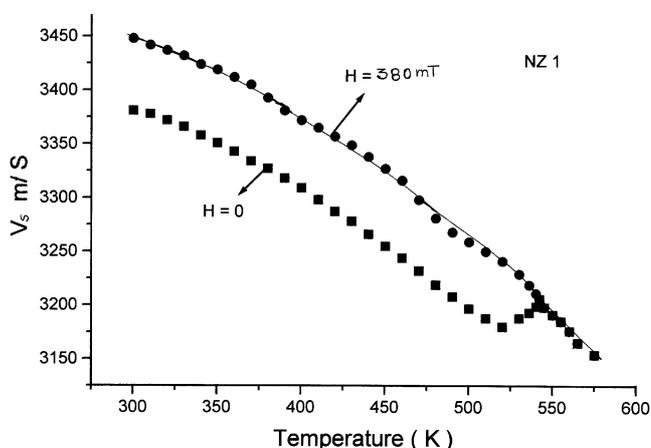


Figure 4. Thermal and magnetic field variations of V_S for NZ-1 ferrites.

$-V_1 (H = 0)$ and $dV_S = V_S (H = 380 \text{ mT}) - (H = 0)$, and are not more than 4% and 2% of the total velocity and varies like the temperature variation of saturation magnetization (M_S) i.e. decreases with an increase of temperature and finally becomes zero at Curie temperature. Similar variation of V_1 on temperature and magnetic field was observed for all the other samples.

In monodomain state the values of V_1 are found to decrease continuously with increasing temperature. This variation of V_1 with temperature (T) can be represented by an exponential equation (Vasudev 1995):

$$V_T = V_0 - B T \exp(T_0/T),$$

where V_0 , B and T are constants. The experimental data have been made to fit with above equation using the standard least-squares method with the help of computer. The values of constants obtained for NZ-1 sample are: $V_0 = 6625 \text{ m/S}$, $B = 3.705 \times 10^{-4} \text{ k/S K}$ and $T_0 = 624 \text{ K}$. On the other hand, a linear equation of the form

$$V_S = V_0 - bT,$$

(where V_0 and b are constants) is used to describe the variation of V_S with temperature. The constants in the above equation for NZ-1 are $V_0 = 3500 \text{ m/sec}$ and $b = 0.588$.

In figures 3 and 4 centres of the dots correspond to the experimental points, while the solid line represents the curves drawn on the basis of above equations. The experimental points are found to lie on the solid line with a maximum deviation of 0.5%.

Figure 5 gives the thermal variation of a_1 measured at zero fields for all samples. It can be seen from the figure that the sample shows a small maximum around 400 K and broad maximum just below the Curie temperature. The rapid increase of a_1 has been extended over 10 K

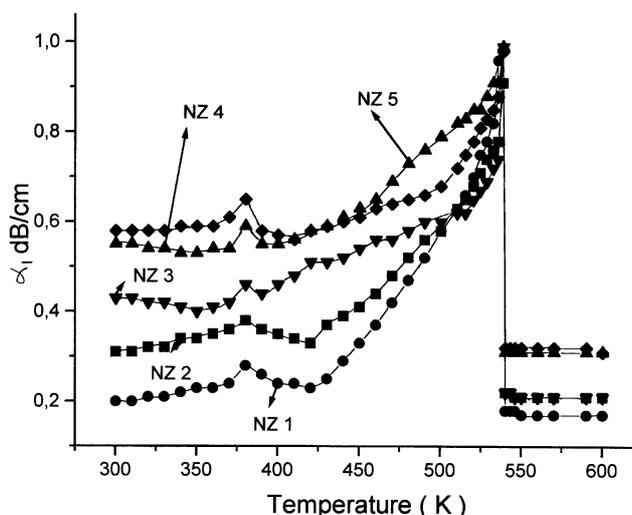


Figure 5. Thermal variation of longitudinal attenuation (a_1) for Ni-Zn ferrites.

below T_c : the very sharp decrease of a_1 from about 0.97 dB/cm down to 0.2 dB/cm is accomplished in less than 2 K. This abrupt change is the signature of the high chemical homogeneity of our samples.

In figure 6, for the sample NZ-1, we present the temperature dependence of a_1 measured both in $H = 0$ and with $H = 380 \text{ mT}$. The value of a_1 in the saturated state is almost temperature independent ($= 0.17 \text{ dB/cm}$), and is equal to the zero field value above T_c , also as expected. Similar variation of a_1 on temperature and magnetic field was also observed for all the other samples.

In all the samples under investigation, it is observed that the temperature corresponding to the peak in the attenuation vs temperature curve is near about the temperature at which both the velocities show maximum value. As the ultrasonic attenuation is the complementary phenomena of the elastic behaviour, as such, the peak observed in a vs T curve can be attributed to the $k_1 = 0$.

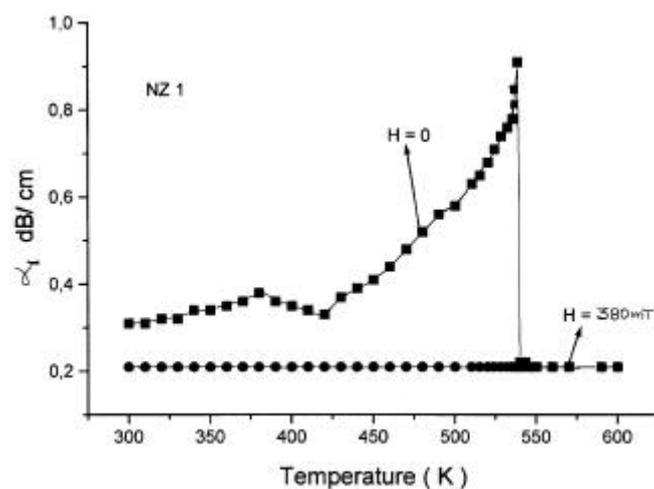


Figure 6. Thermal and magnetic field variation of a_1 for NZ-1 ferrites.

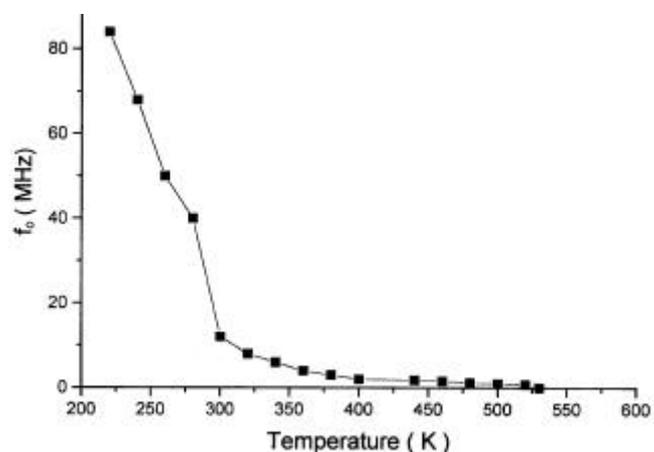


Figure 7. A plot of f_0 vs temperature (T).

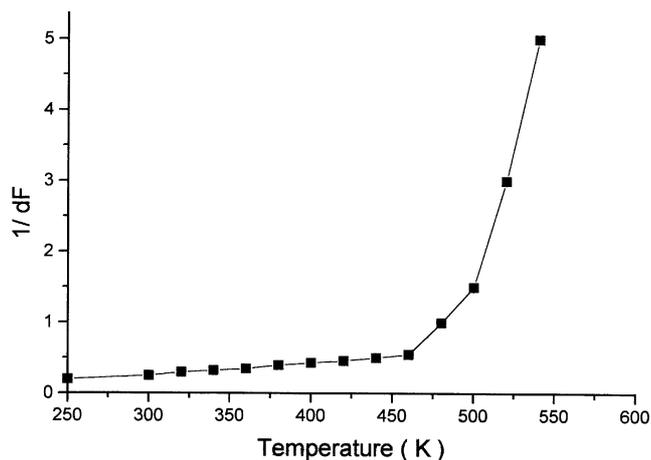


Figure 8. Thermal dependence of relative frequency distance ($1/dF$).

The effects of microstructure are well marked on the attenuation but they are not as dominant as for the velocity. It can be seen from figures 7 and 8, the microstructure contribution to a_1 is of the order of 95% of the total (when compared to more than 30 to 40% on V_1). The substantial magnetic contribution to a_1 seems to result from two contributions: an electronic diffusion related magnetoelastic interaction in the 400 K region and interaction of ultrasonic waves with the domain walls in the vicinity of T_c . We know that the ferrites exhibit magnetic after-effects due to small deviations from the stoichiometry, and the relaxation time of which falls in the microsecond range above room temperature; consequently a 1 MHz ultrasonic wave (1 μ s period) can induce—through the magnetoelastic coupling—spin rotations or domain wall movements, which leads to electronic migrations: this can explain the relative maximum of a_1 observed around 400 K.

An initial permeability (Guyot *et al* 1989) studies were made on same sample and found that the relaxation frequency (f_{DW}) of the domain walls decreased down to MHz range before T_c (figure 7) with an increase of temperature. Figure 8 gives a plot of relative frequency distance (dF) vs temperature and is given by

$$1/dF = F_{US}/F_{DW} - F_{US} = 1/F_{DW} - 1,$$

where F_{US} is the relaxation frequency of the ultrasonic waves and the same was obtained from the frequency variation attenuation (Papaiah 1992). The quantity (dF) has a non-negligible value only very close to T_c and similar sharp temperature dependence as that of a_1 close to T_c . In other words, the absorption of ultrasonic waves and the relaxation of domain wall in the same frequency range are mirror effects: the domain wall can couple to

absorb adapted frequency of ultrasonic waves or relax through the emission of elastic waves. Further, detailed studies are in progress on different ferromagnetic oxides to understand this problem.

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