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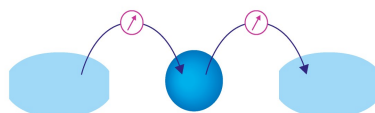
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Magnetic Aftereffects in Ferrimagnetic Oxidic Spinels

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The typical aftereffect spectra of ferrites and related oxides could usually be classified as due to either ionic (and vacancy) or electron processes. The present status of the study of these phenomena is outlined especially from the point of view of the underlying microscopic mechanisms. As an illustration, the results obtained with Mn-Fe and Mn-Cu-Fe oxidic spinels are presented. The magnetic-loss spectra were studied in a broad temperature range from 2° to 360°K and some additional measurements of induced anisotropy and permeability disaccommodation were performed. The role played in magnetic aftereffect by various valency states of the ions present is compared with electrical conductivity measurements. Three distinct relaxation bands of basically electronic origin were found in Mn-Fe spinels. The corresponding $\tan\delta$ maxima for 10⁵ Hz frequency range were situated at $\lesssim 2^\circ\text{K}$, 10°-50°K, and 90°-350°K, respectively, the exact temperature and related activation energies depending on the composition. These relaxation processes were ascribed successively with descending temperature to reorientations of Jahn-Teller distortions induced by Mn³⁺ ions stabilized by means of trapped electrons, to ordering of Fe-ion valencies by means of electron transfer, and to reorientation of unstabilized Jahn-Teller distortions of Mn³⁺ occupied octahedra.

I. INTRODUCTION

The rate with which a magnetic system relaxes towards its thermal equilibrium may differ widely depending on the kind of relaxation processes, temperature, etc. From a rather broad variety of possible relaxation mechanisms we shall confine ourselves to those which are in some way related to inner rearrangements in the lattice and very often exhibit the characteristics of a diffusion process. This implies a strong temperature dependence of the characteristic relaxation time (usually of the exponential type) so that the relaxation may become relatively slow at least in some temperature range. The terms "diffusion aftereffect" or aftereffect of "Richter type" are often used as synonyms for labeling these processes. The presence of such a slow relaxation process in a magnetic material may have serious and usually undesirable consequences for its properties from which, e.g., permeability disaccommodation and other ageing effects, or magnetic losses are most frequently mentioned. On the other hand the existence of the diffusion aftereffect enables the so-called magnetic annealing to occur. This provides a very useful way for obtaining or improving some important characteristics of magnetic materials such as rectangularity or constriction of the hysteresis loop. For these reasons, as well as for useful information yielding to the physical research of magnetics the study of the aftereffects is still subject to a lively interest of both physicists and technicians.

The aftereffect of this type was discovered in iron containing some impurities (C, N); Snoek was the first who related this phenomenon to the diffusion of the impurity atoms embedded interstitially in the lattice and who later discovered similar aftereffects in ferrites.¹

¹J. L. Snoek, *New Developments in Ferromagnetic Materials* (Elsevier Publishing Co., Inc., New York, 1947).

A rigorous theoretical treatment was given by Néel² who was also able to show that the anisotropic coupling of the magnetization vector to the local order in the lattice (which is responsible for the after-effects) is in principle of the same origin as the magnetocrystalline anisotropy. This statement intimately relates the after-effects to the induced anisotropy and the magnetic-annealing effect. Although Néel's theory was elaborated for the special case of α -iron with carbon as an impurity, it forms a proper general basis also for studying the aftereffects in other substances. On the other hand, the microscopical mechanisms which usually form a common basis for both induced anisotropy and various aftereffects are more specific for a given class of materials so that it proves to be useful to discuss them separately for alloys, metals with impurities, oxides, etc.

The aim of this paper is to give a consistent discussion of the temporary state of our knowledge concerning the microscopical mechanisms of the after-effects in oxidic spinels; some of the concepts will then be illustrated by the results we have obtained with the systems of Mn-Fe and Cu-Mn-Fe spinels.

II. VARIOUS AFTEREFFECTS AND THEIR ORIGIN

We can define a microscopical state of the specimen by specifying the spatial distribution and the state of all its constituents as atoms, ions (including the state of outer electrons), and also, for the sake of convenience, ionic vacancies or other defects. Let us call such microstates "configurations." In thermal equilibrium, a certain probability independent of time may be ascribed to each configuration which determine the macroscopical properties of the specimen. Quite generally, a magnetic relaxation or aftereffect connected with some

²L. Néel, *J. Phys. Radium* **13**, 249 (1952).

inner rearrangements in the crystal may take place if (a) some configurations exist which are degenerate or nearly degenerate in the absence of magnetization but become energetically nonequivalent when it is present, and (b) the transition of one configuration to another is possible at reasonable time.

The free enthalpy of a magnetic crystal may be written in the form

$$G = G_0 + \int (g_{\text{ex}} + g_a + g_{\text{me}} - \mathbf{M} \cdot \mathbf{H}) dv, \quad (1)$$

where G_0 does not depend on the magnetic state of the crystal and g_{ex} , g_a , etc., represent the familiar expressions for the densities of exchange, magnetocrystalline, magnetoelastic and magnetostatic energies, respectively.

Now it is seen that according to the assumptions (a) and (b), G (and $G - G_0$ as well) depends on both $\mathbf{M}(\mathbf{r})$ and the actual inner arrangement of the crystal and hence any change of the external conditions, especially field \mathbf{H} , will generally induce changes in both magnetization vector distribution and local arrangements in the lattice towards a new equilibrium state. In this way a lag of magnetization behind the magnetizing field occurs which is the common basis of all after-effects discussed here. The rate of relaxation of $\mathbf{M}(\mathbf{r})$ is determined by the slower process which usually is the rearrangement in the lattice necessary for minimizing the free enthalpy. These rearranging processes are realized by successive transitions between different configurations and will be characterized by certain spectrum of relaxation times which may be either discrete (with one or larger number of relaxation times) or continuous. A quite generally formulated theory of the relaxation problem of this kind was given by Iida.³

Although all terms of the integrand in (1) might in principle contribute to the magnetic after-effect usually the contribution of g_a , corresponding to the induced anisotropy, is only considered.⁴ We will do the same without further notion. For cubic crystals the contribution of induced anisotropy to g_a can be expressed in the familiar form

$$\Delta g_{ai} \equiv g_{aV} = -F \sum \alpha_i^2 \beta_i^2 - G \sum \alpha_i \alpha_j \beta_i \beta_j, \quad (2)$$

where α_i , β_i are directional cosines of magnetization vector during annealing and measuring, respectively.

The most important of the relaxation effects that can arise in this way are given in Table I. A direct measurement of the induced anisotropy is most preferable for a quantitative evaluation although the rotational hysteresis seems also to be suitable for this purpose. The evalu-

TABLE I. Summary of main after-effects.

Effect	Physical characteristics
Induced-anisotropy relaxation	Time variation of the induced anisotropy in magnetically saturated samples after changing the field orientation.
Rotational hysteresis and losses	Attenuation of uniform rotation of sample due to the induced-anisotropy torque.
Ferromagnetic resonance line broadening	Damping of the uniform precession; maxima on ΔH vs T curves depending on frequency.
Permeability disaccommodation	Time decrease of μ due to domain wall stabilization.
Magnetization viscosity (creeping)	Time increase of magnetization due to wall destabilization after switching on magnetizing field.
Time changes of hysteresis loop, its constriction and rectangularity	Stabilization and destabilization effects of walls and magnetization, dynamical rectangularity.
Magnetic losses	Wall relaxation; maxima in both $\tan \delta$ vs T and $\tan \delta$ vs ω dependencies.

ation of other effects is not so straightforward, many of them depending on the domain structure which is usually not exactly known. Nevertheless they are very often successfully used for obtaining, e.g., the spectra of relaxation times or a qualitative picture of relative magnitudes of various relaxation processes involved.

The relation of the listed effects to the induced anisotropy follows from the general theory of Néel⁵ and subsequent works.^{5,6a} As our discussion includes, besides induced anisotropy and disaccommodation data, also $\tan \delta$ measurements the use is made of our work^{6a} where the problem of the wall relaxation was solved without the usual restrictions concerning the intensity of the aftereffect and which form a more realistic basis for a quantitative evaluation. For details the reader should consult the original papers.

From the general outline we have given in this section it can be also concluded which type of information can be obtained from magnetic aftereffect studies, namely (1) information about local arrangement, magnitude of elementary anisotropic interactions and their origin, (2) information about the kinetics of rearranging processes and related relaxation spectra, and (3) additional information about magnetization processes and how they are influenced by the presence of the induced anisotropy and aftereffect stabilization.

³ S. Iida *et al.*, J. Phys. Soc. Japan **17**, B-I, 282 (1962); *ibid.* **21**, 2505 (1966).

⁴ Let us note, that the Snoek's original interpretation of the diffusion after-effect was essentially based on the contribution of magnetoelastic energy g_{me} .

⁵ A. M. Clogston, Bell System Tech. J. **34**, 739 (1955); P. Brissonneau, Compt. Rend. (Paris) **244**, 1174 (1957); J. Phys. Chem. Solids **7**, 22 (1958); J. Appl. Phys. **29**, 249 (1959); J. F. Janak, J. Appl. Phys. **34**, 3356 (1963); E. Kratochvílová, Czech. J. Phys. **B15**, 901 (1965).

^{6a} S. Krupička and V. Roskovec, Czech. J. Phys. **B16**, 99 (1966); V. Roskovec (to be published).

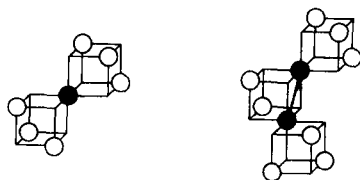


FIG. 1. Simplest ionic configurations of octahedral cations in the spinel lattice.

In the following sections the first two aspects are discussed in connection with oxidic spinels. As an example of the point (3) let us mention, e.g., the work by Kratochvílová^{6b} who derived the distribution of critical fields for the system of Bloch walls in an Mn-Fe spinel from the aftereffect data.

III. PRESENT STATUS OF THE STUDY OF MAGNETIC AFTEREFFECTS IN OXIDIC SPINELS

In the oxidic ferrimagnetic spinels induced anisotropy and the aftereffects are usually connected with the processes taking place in the octahedral (or simply B) sublattice. In an ideal (normal) spinel the local symmetry of each B site is trigonal with the axis parallel to one of the body diagonals (Fig. 1). Thus we have four categories of B sites which become nonequivalent when the magnetization is present. The unequal distribution of Co^{2+} among these four kinds of sites and the induced anisotropy produced by such an arrangement is a well-known result of magnetic annealing in many Co-containing magnetic spinels. On the other hand many spinels of interest are not normal but wholly or partly inverse. In such a case ions with different valencies are more or less randomly distributed among the octahedral sites so that the actual local symmetry is lowered and made to fluctuate in an irregular way.

Thus in general, even if we still consider only the simplest configurations such as isolated cations or pairs of active cations, their anisotropic contribution will depend on the whole array of neighboring ions and their arrangement. This reveals the importance of a short-range order (especially in inverse spinels) for the problems of induced anisotropy and its relaxation as was recognized by Iida. The simplest clusters of B cations which should be considered in the case of active single ions and pairs, following Iida,³ are given in Fig. 1.

With respect to the nature of the rearranging processes we can divide the phenomena to be discussed (rather arbitrarily) into two groups, namely (1) electronic processes and (2) ionic processes. An ionic process is characterized by the change of core distribution while during an electronic process the ion cores retain their lattice position and only small eventual displacements are allowed. The latter may be, e.g., the case of Jahn-Teller-distortion-induced anisotropy as discussed in Sec. IV.

1. Electronic Processes

If ions of a certain kind coexist in different valency states on equivalent sites in the lattice an electron transfer is sufficient to rearrange the valencies and to create a local order responsible for induced anisotropy and stabilization effects. The well-known example is found in many ferrosinels having both ferrous and ferric ions in octahedral positions (e.g., iron-rich Mn, MnZn, Ni, NiZn, and Mg ferrites).⁷⁻¹³ It is believed that this electron-transfer mechanism is the same as that responsible for the electrical conductivity in these substances and the agreement between activation energies deduced from electrical measurements and magnetic aftereffect is usually used to support this conclusion. In many cases of Fe^{2+} containing spinels the activation energies from both $\tan\delta$ and electrical conductivity are of the order of 10^{-2} to 10^{-1} eV. If Fe^{2+} ions are present in a very small concentration only, e.g., in slightly reduced samples having nominally stoichiometric cation ratio of one divalent cation to two ferric ions, the activation energy may be appreciably higher and $\tan\delta$ maxima lower and shifted to higher temperatures. This can be naturally explained in the framework of the Fermi-Dirac statistics applied to the electron-hopping mechanism^{14,15} as due to a contribution of thermally activated electrons from lower-lying levels. These may be the Fe^{2+} levels localized in the vicinity of some lattice defects or simply levels belonging to other ions present, e.g., Ni^{2+} . An alternative but actually rather similar explanation was given by Kienlin.⁸

As there exist only few direct measurements of the induced anisotropy connected to the valency ordering of the iron ions, it is difficult to discuss the origin of the anisotropic coupling. Nevertheless, it is believed that Fe^{2+} is the active ion due to its large single-ion anisotropy contribution and further that the local ordering may be of a similar type as the long-range order in magnetite at low temperature giving the induced anisotropy of the "F" type. Anisotropy of this type was experimentally found by Menyuk and Dwight¹⁰ in Ni ferrites. At sufficiently low concentration of Fe^{2+} ions there might arise also G-type anisotropy, caused by the one-ion contribution of these ions in trigonal field. Experimental data supporting this possibility are to our

⁷ H. P. J. Wijn and H. van der Heide, *Rev. Mod. Phys.* **25**, 98 (1953).

⁸ A. v. Kienlin, *Z. Angew. Phys.* **9**, 245 (1957).

⁹ D. Köhler, *Z. Angew. Phys.* **11**, 103 (1959).

¹⁰ N. Menyuk and K. Dwight, *Phys. Rev.* **112**, 397 (1958); *J. Appl. Phys.* **30**, 36S (1959).

¹¹ A. Marais and T. Merceron, *Compt. Rend. (Paris)* **239**, 2511 (1959).

¹² K. Závěta *et al.*, *Phys. Status Solidi* **14**, K9 (1966).

¹³ A. Broese van Groenou, *J. Phys. Chem. Solids* **28**, 325 (1967); See also A. Broese van Groenou and R. F. Pearson, *ibid.* **28**, 1027 (1967).

¹⁴ G. H. Jonker and S. van Houten, *Halbleiterprobleme VI*, Vieweg, Braunschweig 1961, p. 118.

¹⁵ F. K. Lotgering, *J. Phys. Chem. Solids* **25**, 95 (1964).

^{6b} E. Kratochvílová, *Czech. J. Phys.* **B15**, 718 (1965).

knowledge still missing. Let us note that aftereffects pointing to the $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ electron exchange have also been found in slightly reduced or doped YIG and LuIG.¹⁶

In addition to iron, other ions may coexist with different valencies in ferrimagnetic spinels, namely Cu, Mn, Co, and others. The situation is complicated by our insufficient knowledge of the exact distribution of valency states.

In some Co-containing spinels the induced anisotropy and magnetic after-effect were found which can be ascribed to the valency ordering of Co^{2+} and Co^{3+} ions. The active ion here is evidently Co^{2+} due to its strong anisotropy¹⁷ the Co^{3+} being supposed to exist probably in the low spin state. The order attained corresponds probably to the preferential occupation of the non-equivalent octahedral sites by Co^{2+} ions. Two cases can be distinguished: (a) The concentration of Co ions on equivalent sites is sufficient for a direct electron exchange $\text{Co}^{2+} \rightleftharpoons \text{Co}^{3+}$. This is, e.g., the case of cobalt-rich Co-Fe and CoFeNi spinels studied by Iizuka and Iida.¹⁸ The activation energy is low ≈ 0.1 eV as it corresponds to the temperature change of carrier mobility only, the situation being similar to iron-rich ferrites with $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ electron exchange. (b) The concentration of both Co^{2+} and Co^{3+} is low so that the electron has to be transported between two more distant Co ions separated by many other ions, e.g., Fe^{3+} . This is the case usually reported.¹⁹ The activation energy is then usually rather high (≈ 0.6 eV) because it includes a creation of a carrier, e.g., $\text{Co}^{2+} + \text{Fe}^{3+} \rightarrow \text{Co}^{3+} + \text{Fe}^{2+}$.

The case of Mn- and Cu-containing spinels is more complicated. A fairly strong aftereffect was reported by many authors if Mn^{3+} or Cu^{2+} ²⁰⁻²² are present and these ions are supposed to be active in this case. Although the mechanism could in principle be similar to that in Co-spinels provided that coexistence with other valencies of respective ions is admitted, another possibility of explanation seems to exist based on the Jahn-Teller effect of Mn^{3+} and Cu^{2+} ions. We transfer the discussion of the system $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+\gamma}$ in more detail to Sec. IV. Let us only note that with Mn^{3+} -containing

spinels the anisotropic coupling may be attributed to the single-ion anisotropy of manganese ions in a tetragonal crystal field and there exists, however, no such simple way in which Cu^{2+} ions could directly contribute to the induced anisotropy. A rather complicated case seems to be the manganese-rich Mn ferrites with small Co addition, studied first by Kienlin and later by Bolšova and Yelkina²³; here a valency exchange among three different kind of ions is possible.

2. Ionic Processes

Into this group the effects having larger activation energy (>0.7 eV) are usually encountered although there seems to be no direct way for proving this conclusion. These effects are usually observable at higher temperatures only (limited from above by T_C) and the direct observation of induced anisotropy and disaccommodation of permeability are most used for their study. We shall discuss separately two types of compounds: (a) ferrites containing Co and (b) ferrites without Co.

In the case of Co-containing systems the anisotropic effect of Co^{2+} ions is strongly prevalent in relation to all other contributions to the induced anisotropy. For low concentration of cobalt we can take into account isolated Co^{2+} and Co^{2+} - Co^{2+} pairs only, as was done by Bickford and Slonczewski.^{17,24} For higher concentrations, however, more complicated multiple configurations will contribute to the anisotropy. The problem of the relaxation-time spectrum which contains three values for low Co-concentrations and becomes rather broad for high ones has recently been discussed in detail by Iida and Miwa.³ The presence of vacancies does not change the magnitude of the anisotropy but the rate of ordering given by the reciprocal relaxation time τ^{-1} is proportional to the vacancy concentration characteristic for the random-walk model of vacancy migration. A rather strong effect of Fe^{2+} upon the activation energy and time constants was reported indicating a possible role of electrons in the arranging process towards charge neutralization as discussed by Yanase²⁵ and Iida.³

The situation for ferrite systems without cobalt is complicated due to the fact that practically all ions present and their various configurations including vacancies can make comparable contributions to the resulting anisotropy. An example of the disaccommodation spectrum for a manganese iron ferrite measured by Marais *et al.*²⁶ is shown in Fig. 2, which is typical of

¹⁶ D. J. Epstein *et al.*, J. Appl. Phys. **32**, 270S (1961); A. G. Gurevič *et al.*, Izv. Akad. Nauk SSSR, Ser. Fiz **25**, 1361 (1961); V. I. Solov'ev, Fiz. Tverd. Tela **6**, 405 (1964); J. H. Judy, J. Appl. Phys. Suppl. **37**, 1328 (1966); R. P. Hunt, *ibid.*, p. 1330; D. I. Tchernev, *ibid.*, p. 1318.

¹⁷ J. C. Slonczewski, Phys. Rev. **110**, 1341 (1958).

¹⁸ T. Iizuka and S. Iida, J. Phys. Soc. Japan **21**, 222 (1966).

¹⁹ K. J. Sixtus, *Solid State Physics in Electronics and Telecommunication* (Academic Press Inc., New York, 1960), Vol. 3, p. 91; A. Marais and T. Merceron, Compt. Rend. (Paris) **248**, 2976 (1959); M. Mizushima, J. Phys. Soc. Japan **18**, 1441 (1963).

²⁰ S. Krupička and F. Vilím, Czech. J. Phys. **7**, 723 (1957).

²¹ S. Krupička, Czech. J. Phys. **B10**, 782 (1960); W. Gieseke, Z. Angew. Phys. **11**, 91 (1959); A. v. Kienlin, Z. Angew. Phys. **11**, 118 (1959); A. P. Greifer and W. J. Croft, J. Appl. Phys. **31**, 85 (1960); E. Kratochvílová *et al.*, Phys. Status Solidi **6**, K23 (1964).

²² A. Marais and T. Merceron, Compt. Rend. (Paris) **261**, 901 (1965).

²³ A. v. Kienlin, *Solid State Physics in Electronics and Telecommunication* (Academic Press Inc., New York, 1960), Vol. 3/1, p. 1; K. M. Bolšova and T. A. Yelkina, Izv. Akad. Nauk SSSR, Ser. Fiz. **25**, 1407 (1961); Fiz. Metal i Metalloved. **17**, 821 (1964).

²⁴ L. R. Bickford, Jr., *et al.*, J. Appl. Phys. **29**, 441 (1958).

²⁵ A. Yanase, J. Phys. Soc. Japan **17**, 1005 (1962); B. Kubota *et al.*, *ibid.* **17**, B-1, 296 (1962).

²⁶ A. Marais *et al.*, Compt. Rend. (Paris) **261**, 2188 (1965).

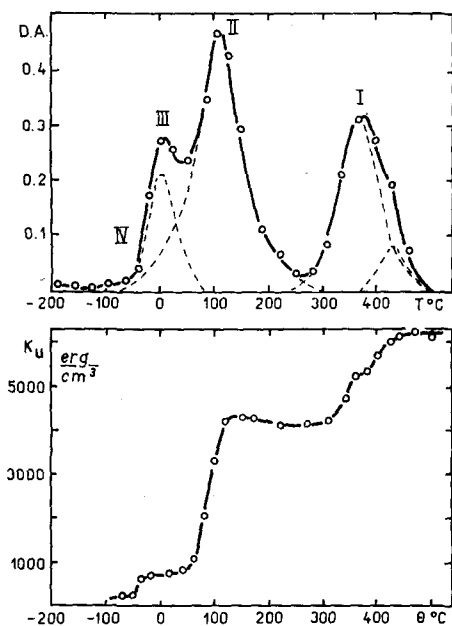


FIG. 2. Disaccommodation of permeability and the induced anisotropy in $Mn_{0.2}Fe_{2.8}O_{4.014}$.²⁶

other iron-rich ferrites too (Ni-Fe, Mg-Fe, etc.). This is one of the rare instances where the induced anisotropy was simultaneously measured and compared with the DA spectrum. Three main peaks I-III of disaccommodation are clearly visible situated at $\sim 380^\circ$, 100° , and 0°C , respectively, with an indication of another process IV at slightly lower temperature. The characteristics of these peaks are dealt with in detail in previous papers^{27,28}; the increase of vacancy concentration usually shifts peaks I and II to lower temperatures (shorter

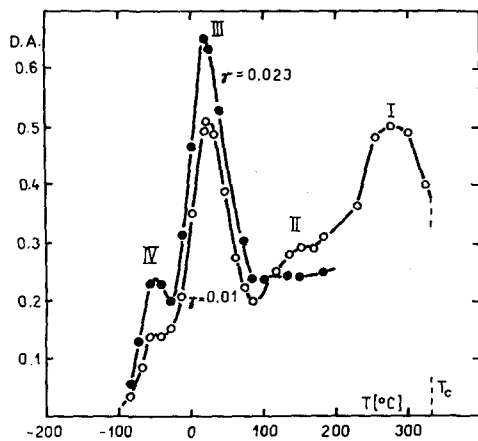


FIG. 3. Disaccommodation spectra for $Mn_{0.85}Fe_{2.15}O_{4+\gamma}$.

²⁷ A. Bragiński *et al.*, J. Phys. Soc. Japan **17**, B-I, 300 (1962); A. Bragiński, Phys. Status Solidi **11**, 603 (1965).
²⁸ S. Krupička, J. Phys. Soc. Japan **17**, B-I, 304 (1962).

relaxation times) while the position of peak III is not affected. The peak IV has only been found in Mn-containing iron-rich spinels; its magnitude increases with the concentration of both Mn-ions and vacancies (Fig. 3) and its existence is conditioned further by the presence of Fe^{2+} ions similarly as process III. Manganese-rich ferrites from the system $Mn_xFe_{3-x}O_{4+\gamma}$ exhibit both DA and induced anisotropy as shown in Fig. 4.²⁹ They are characterized by the absence of peak III and IV. We have found similar DA spectra also in $Cu_xMn_yFe_{3-x-y}O_{4+\gamma}$ ferrites.

Most complete data concerning the induced anisotropy are available for the $Ni_xFe_{3-x}O_4$ system including its end member Fe_3O_4 . Magnetite is a particularly suitable object for discussing the mechanisms of anisotropy as it contains only one kind of cation (from the point of view of ion migration) and a certain concentration of vacancies. Hence, the anisotropic distribution of the latter is the only possible basis for explaining the induced anisotropy and DA of the ion-migration type.

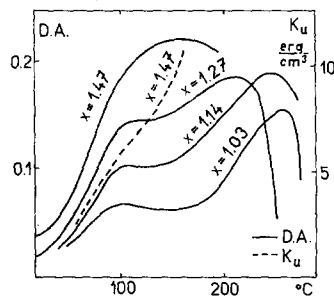


FIG. 4. Disaccommodation spectra for manganese-rich ferrites $Mn_xFe_{3-x}O_{4+\gamma}$.²⁹

Various peaks in the DA would correspond to different arrangements of vacancies and the underlying modes of vacancy migration. The DA spectrum of magnetite²⁷ contains all the three peaks mentioned earlier although their magnitudes are modified. The induced anisotropy measured by Knowles³⁰ for peak III in Fe_3O_4 was of the G type which is compatible with the preferential occupation of nonequivalent B sites by vacancies. The magnitude of G at room temperature gives the energy per cation vacancy $W = 2.3 \times 10^{-16}$ erg, in fair agreement with the value obtained by Yanase from the dipolar contribution of such a vacancy ordering. There may, however, exist another contribution not yet considered which is due to the fact that the presence of a vacancy in one of the four types of B sites enhances the probability of occupying the next-nearest B sites of the same kind by Fe^{2+} ions. This anisotropy would be approximately equal to $w \approx (4/3)KU(Fe^{2+}) - (7/3)KU(Fe^{3+})$ per vacancy. In magnetite this mechanism probably

²⁹ S. Krupička, Czech. J. Phys. **B14**, 29 (1964); A. Bragiński and S. Siermiński, Phys. Status Solidi **17**, K211 (1966).

³⁰ J. E. Knowles, Proc. Intern. Conf. Nottingham (1965), p. 619.

makes a small contribution but might be more effective with lower Fe^{2+} concentrations.^{30a}

In mixed crystals the presence of another cation (e.g., Ni^{2+} , Mg^{2+} , etc.) makes possible more complicated arrangements of two types of cations where vacancies may play either active or intermediating role. The latter case is supposed to take place in the high temperature effects (especially I) as follows from the shortening of relaxation times with increasing vacancy concentration both in disaccommodation^{27,28} and induced anisotropy measurements.³¹ This conclusion is also supported by the magnitude of this effect upon the vacancy concentration.^{27,31} The dependence upon Fe^{2+} concentration³² may be explained by the possibility that moving electrons can temporarily convert preferentially oriented Fe^{3+} - Fe^{3+} pair into Fe^{2+} - Fe^{2+} and thus enhance the induced anisotropy. The behavior of process III in mixed crystals is characterized by (a) independence of its temperature position both on vacancy concentration and the kind of the other ion, (b) a linear dependence of its magnitude upon the product of vacancy concentration and the concentration of some other ion present, and (c) the presence of the $-F$ term in induced anisotropy in addition to the G term,³³ found in magnetite (at least in some cases). These characteristics make possible the conclusion that process III also contains pair ordering, where one constituent of the pair is the vacancy and that for this ordering vacancy motion on short distances is responsible.

When concentration of both vacancies and ferrous ions are comparable the magnitude of this effect is proportional to their product, i.e., $(c_{\text{Fe}^{2+}})(c_{\square})$.^{28,34} If $c_{\text{Fe}^{2+}}$ approaches zero, the peak is shifted to higher temperatures indicating a supporting role of electron transfer in the vacancy migration. This is in accord with the absence of peak III in manganese-rich ferrites.²⁹

IV. ELECTRONIC RELAXATION IN Mn-Fe AND Mn-Cu-Fe SPINELS

1. Experimental Results on $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+\gamma}$ System

For a long time it was suspected that the magnetic aftereffect due to electronic processes is intimately bound to the electric-conduction mechanism.^{7,8,35} As

^{30a} It seems at the first sight, that the effect of Fe^{2+} ions should be large due to their strong L - S coupling. But Yoshida and Tachiki, *Progr. Theoret. Phys. (Kyoto)* **17**, 331 (1957), when analyzing the cubic anisotropy of magnetite showed that the contribution of Fe^{2+} ions is relatively small and probably determined by the cubic splitting parameter a rather than by the second-order effect of the trigonal field. This fact was ascribed to the fast electron migration and associated rapid fluctuations of the crystal field (J. Kanamori, *J. Phys. Soc. Japan* **17**, B-1, 271 (1962)).

³¹ K. Motzke, *Phys. Status Solidi* **2**, K52, K307 (1962); **4**, K13 (1964).

³² N. L. Brjukhatov *et al.*, *Czech. J. Phys.* **B17**, 347 (1967).

³³ E. M. Gyorgy *et al.* (private communication).

³⁴ A. Marais and T. Merceron, *C. R. Acad. Sci. Paris* **257**, 1760 (1963).

³⁵ S. Krupička and K. Závěta, *Czech. J. Phys.* **9**, 324 (1959).

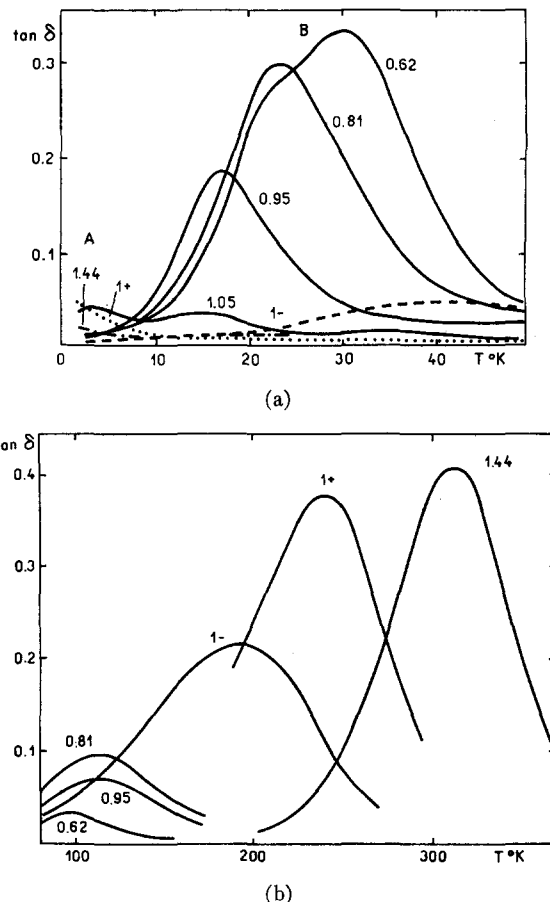


FIG. 5. Magnetic losses vs T for $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+\gamma}$ system. Figures show Mn concentration x , $1+$ and $1-$ corresponds to oxygen excess and deficit, respectively.

our knowledge of the electrical properties of Mn-Fe spinels is relatively deep,^{15,36,37} they represent a suitable subject for verifying this idea. For this purpose new measurements of $\tan\delta$ spectra in a broad temperature range from 2° to 350°K were undertaken in order to complete the earlier data on $\text{Mn}_x\text{Fe}_{3-x}\text{O}_{4+\gamma}$ system.^{20,38} The polycrystalline samples with x ranging from 0.6 to 1.66 were prepared in usual ceramical way, and in addition to the cation ratio and oxygen stoichiometry expressed by γ were also checked by the chemical analysis. The complex permeability $\mu = \mu' - i\mu''$ was measured at frequencies reaching from 75 to 600 kHz. Preliminary results of this study were already published¹² and experimental details will appear elsewhere.

Let us summarize the main experimental results. In the temperature range used we were able to distinguish three processes giving well-distinct maxima on the magnetic loss vs temperature plots as seen in Fig. 5.

³⁶ K. Závěta, *Czech. J. Phys.* **9**, 748 (1959), Z. Šimša, *ibid.* **B15**, 435 (1965); **B16**, 919 (1966).

³⁷ Z. Šimša, *Czech. J. Phys.* **B15**, 435 (1965); **B16**, 919 (1966); *J. Phys. Chem. Solids* (to be published).

³⁸ R. Gerber *et al.*, *Phys. Status Solidi* **16**, 795 (1966).

TABLE II. Data for process B in $Mn_xFe_{3-x}O_{4+\gamma}$.

x	γ	ϵ_M (meV)	T_m (°K)	$\log \tau_\infty$	$\Delta(1/\mu)T$
0.62	-0.01	21	30.2	-9.5	2.4
0.81	-0.003	17	23.4	-9.6	0.9
0.95	+0.004	13	17	-9.8	0.5
1.00	-0.005	30	40	-9.8	...
1.02	+0.013	20-30	33
1.05	+0.008	10-15	12-13

The first process denoted by A, takes place at temperatures lower than $\approx 4^\circ\text{K}$, the next process, B, between 10° and 50°K , and the third C, between 90° and 350°K . From the frequency shift of the temperature where $\tan\delta$ reaches its maximum the activation energy ϵ_M was derived assuming the validity of the Arrhenius relation

$$\tau = \tau_\infty \exp(\epsilon_M/kT). \quad (3)$$

Although τ is not exactly equal to ω^{-1} the error in determining ϵ_M from (3) taking $\omega\tau=1$ is almost always negligible.^{6a}

Process A was only found for manganese-rich part of the system and with the exception of one case its maximum lay below our lowest temperature, i.e., 2°K . Process B is present quite distinctly for $x < 1$ with values of $\tan\delta_{\max}$ of the order of 10^{-1} and for x slightly exceeding 1 its presence is only slightly indicated in some cases with values of $\tan\delta_{\max}$ on one order lower. The values of activation energies together with temperatures T_m at which $\tan\delta$ reaches its maximum at 150 kHz are given in Table II. The extrapolated τ_∞ from (3) are practically of the same order of 10^{-10} - 10^{-9} sec. Process C was found with all measured samples; it is rather weak for iron-rich compositions but rises steeply when x passes 1. For $x > 1$ its intensity seems to follow the magnitude of μ' corrected for the expected contribution of the rotational processes which show practically no relaxation.

Activation energies ϵ_M follow a similar dependence on x with values approx. 0.1 eV higher than those derived from the electrical conductivity, i.e., ϵ_σ (Fig. 6). The larger difference between ϵ_M and ϵ_σ for $x \approx 1$ was also found in earlier measurements³⁵ where both activation energies were determined from the same sample. The τ_∞ values for this process are comparable to τ_∞ of process B for $x \leq 1$ but with higher x they decrease to the value $\approx 10^{-13}$ sec. The form of $\tan\delta$ curves indicates that the relaxation time spectrum for both B and C processes is rather broad and a more detailed analysis based on the logarithmic distribution of activation energies⁶ gave $\Delta\epsilon/\epsilon = 0.3$ and 0.1 for typical curves for B and C, respectively.

The stabilization energy W_0 of the Bloch wall which characterizes the intensity of its relaxation is given by^{2,6}

$$\begin{aligned} W_0 &= cw^2/\xi kT \propto \Delta(1/\mu)M_s^2 \\ &= 2[\xi^2 + (g^2 + g^4)^{1/2}]\mu_0^{-1}M_s^2 \end{aligned}$$

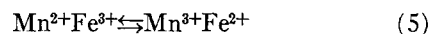
for

$$w \ll kT \quad \text{and} \quad g = \tan\delta_{\max}, \quad (4)$$

where c is the concentration of the active configuration (single ion, ionic pair etc.), w its anisotropic energy, ξ a numerical factor depending upon the type of anisotropic coupling; k , T , and M_s have the usual meaning. $\Delta(1/\mu)$ is the difference between reciprocal values of the relaxed and unrelaxed permeability μ_0 . Relative values of the quantity $\Delta(1/\mu)T$ proportional to cw^2 (M_s is practically independent of x in the compositions considered) are given in Table II for process B. For process C, however, this estimate could not be done due to the narrow frequency range of our measurements and to strong temperature dependence of μ_0 . Our estimates of W_0 were based on the last expression in (4) from which we obtained an increase of W_0 with increasing manganese content up to $x=1$; for higher x the spread becomes so large that the concentration dependence of W_0 could not be determined.

2. Discussion

First of all, let us briefly mention the known data on the distribution of ions and their valencies in the system $Mn_xFe_{3-x}O_4$. As demonstrated by neutron diffraction³⁹ our system displays a gradual change between an inverse spinel for $x=0$ and a normal one for $x=3$, giving for stoichiometric Mn-ferrite approximately 80% normal spinel. For the valency state of Mn in B sites for $x \approx 1$ two possible models were proposed^{15,35,37,40} in which the equilibrium between



is supposed to lie either to the left- or the right-hand side. The latter possibility is supported by the NMR experiment of Kubo *et al.*⁴¹ who found some Mn^{3+} on B sites at low temperatures for $x=1$ and will be adopted here. For explaining the electrical-conductivity data from this model, it is necessary to postulate the existence of strongly coupled Mn^{3+} - Fe^{2+} pairs with an energy of about 0.3 eV for releasing the electron from this pair.

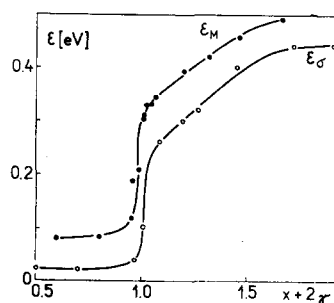


FIG. 6. The dependence of activation energies of magnetic relaxation ϵ_M and electrical conductivity ϵ_σ on Mn concentration for $Mn_xFe_{3-x}O_{4+\gamma}$.

³⁹ J. M. Hastings and L. M. Corliss, *Phys. Rev.* **104**, 328 (1956), I. I. Yamzin *et al.*, *J. Phys. Soc. Japan* **17**, B-III, 55 (1962).

⁴⁰ F. W. Harrison *et al.*, *Phys. Rev.* **106**, 865 (1957).

⁴¹ T. Kubo *et al.*, *J. Phys. Soc. Japan* **22**, 679 (1967).

This stabilization energy may be attributed to the Jahn–Teller effect. In this way all Fe^{2+} ions for $x \geq 1$ are bound to Mn^{3+} and for $x < 1$ we get no unpaired Mn^{3+} . The increase of ϵ_r with $x > 1$ together with Seebeck-effect measurements on quenched samples³⁷ lead to the hypothesis that electrons on Fe^{2+} ions are more strongly bound with increasing x due to Mn^{3+} cluster formation.

The behavior of process A, first of all, its sharp disappearance for $x < 1$ resembles the concentration dependence of “free” (i.e., unpaired) Mn^{3+} ions. The very low temperature and expected low activation energy (of the order of 10^{-3} eV) suggest a connection to the mechanism proposed by Gyorgy *et al.*⁴² for the interpretation of mechanical losses in oxides containing ions with a strong Jahn–Teller effect, and probably is of the same origin as the acoustic losses observed by Gibbons⁴³ in Mn-rich manganese ferrite below 2°K. Hence it can be presumably ascribed to the reorientation of the locally distorted Mn^{3+} occupied octahedra, which are not stabilized by a trapped electron or for any other reason (e.g., by stabilizing effect of cation vacancies and other Mn^{3+} ions). Let us note that our process A is probably not due to the mechanism used by Clarke⁴⁴ when discussing the origin of low-temperature FMR line broadening in Mn ferrites because of the disagreement of the experimental relaxation times.

Process B can naturally be related to the ordering of Fe^{2+} by means of the collective rearranging of electrons. Both its magnitude, as expressed by the quantity $\Delta(1/\mu)$ given in Table II, compared to the concentration of free Fe^{2+} ions and the relatively high common value of τ_∞ points to this interpretation. Also the activation energies for this process are in a reasonable agreement with ϵ_r values found for iron-rich ferrites when the electrical conductivity was measured in the same low-temperature region.⁴⁵ The values of ϵ_M are increasing with rising Fe^{2+} content together with the $\tan\delta_{\max}$ temperatures. This behavior is ascribed to the increasing interaction between free electrons. Comparable magnitudes of ϵ_M have been recently observed by van Groenou⁴³ for Mn and Mn–Zn ferrites but his interpretation is quite different. Mizushima and Iida⁴⁶ observed a peak in the temperature dependence of dielectric losses at 9.3 GHz of manganese ferrites with $x \approx 1$. This effect clearly associated with electron motion could be brought into agreement with our process B if we admit a slight temperature dependence of activation energy.⁴⁵ Also the FMR line broadening found in our laboratory for manganese ferrites with slight excess of iron at 150°–300°K⁴⁷ could be interpreted in terms of this process.

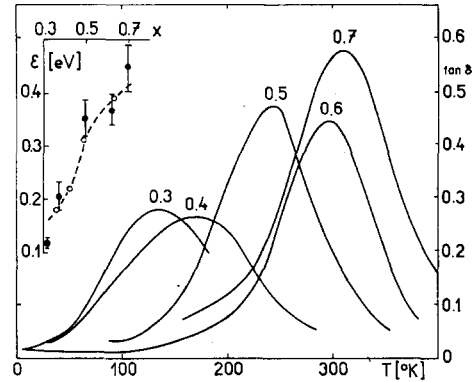


FIG. 7. Magnetic losses vs T for $\text{Cu}_{0.8}\text{Mn}_x\text{Fe}_{2.5-2}\text{O}_{4+\gamma}$ system. Insert shows the dependence of activation energies of magnetic relaxation (●) and electrical conductivity (○) on Mn content x .

The interpretation of process C is more complicated due to its apparently contradictory behavior. Its magnitude is rising with Mn content similarly as the induced anisotropy^{38,48} and is in a certain sense complementary to process B as seen from Fig. 5. From this fact we have to connect it to Mn ions and most probably in the trivalent state. On the other hand the agreement of the concentration dependences of ϵ_M for this process and ϵ_r forces us to take into account the role of electron transport in its mechanism too. But if we take the valency exchange $\text{Mn}^{2+} \rightleftharpoons \text{Mn}^{3+}$ for the source of the effect C then the related induced anisotropy should be limited for larger $x > 1$ by the slightly decreasing concentration of Mn^{2+} in contradiction to experimental results.^{38,48} Therefore we propose a model which combines the anisotropic effect of local distortions induced by Mn^{3+} ions with a reorientation and/or stabilization effect of electrons which are also responsible for the transport phenomena. We suppose that if a distortion stabilized by an electron on a neighboring Fe ion should change its direction under the influence of the magnetization, the electron has to be removed from its stable position and placed at another one. This can be assisted by the electrons carrying the electrical current and thus involves similar thermal activation as the transport itself (eventually plus an extra energy connected with the reorientation process). The detailed process could, e.g., correspond to a two-electron scattering where an additional electron approaches the stabilized Mn^{3+} – Fe^{2+} pair (or cluster) creating a situation favorable for the release of the electron from the stabilized position. For $x < 1$ this may be accomplished by the quasi-free electrons on the Fe lattice and hence with low activation energy while for $x > 1$ each carrier must be created by thermal activation. With this mechanism the role of Mn^{3+} clustering^{37,49} must also be considered, but the experiments in this direction are unfortunately not yet

⁴² E. M. Gyorgy *et al.*, J. Appl. Phys. **37**, 1303 (1966).

⁴³ D. F. Gibbons, J. Appl. Phys. **28**, 810 (1957).

⁴⁴ B. H. Clarke, J. Phys. Chem. Solids **27**, 353 (1966).

⁴⁵ K. Závěta (to be published in Czech. J. Phys. B.)

⁴⁶ K. Mizushima and S. Iida, J. Phys. Soc. Japan **22**, 1300 (1967).

⁴⁷ Z. Smetana, (private communication).

⁴⁸ P. D. Baba and E. M. Gyorgy, J. Appl. Phys. **38**, 909 (1967).

⁴⁹ J. B. Goodenough, J. Appl. Phys. **36**, 2343 (1965); D. B. Rogers *et al.*, *ibid.* **36**, 2338 (1965).

finished. Let us note that vacancies can provide a similar stabilizing effect upon Mn^{3+} distortions⁵⁰ as electrons do. The electron-assisted migration of these vacancies may explain DA peak IV for $x < 1$ (Figs. 2 and 3), classified as an ionic one, as well as that situated at approx 100°C for $x > 1$ (Fig. 4) in close analogy to our interpretation of the electronic process for both $x < 1$ and $x > 1$.

The contribution to the anisotropic coupling of the ions present in the distorted areas of the crystal may be of various origins: single-ion contribution particularly of Mn^{3+} ions, dipolar energy for larger clusters and/or various types of pair, or cluster interactions as will be discussed elsewhere.

3. $\text{Cu}_{0.5}\text{Mn}_x\text{Fe}_{2.5-x}\text{O}_4$ System

In Fig. 7 representative $\tan\delta$ vs T curves are given together with the plots of the composition dependencies of ϵ_M and ϵ_σ . In all cases only one peak of $\tan\delta$ was observed which for $x > 0.5$ can be apparently ascribed to an analogous process used for explaining C in Mn-Fe spinels. For $x < 0.5$ we may guess from the asymmetry of the peak that both effects, B and C, are accidentally displayed in the same temperature region and superposed, one increasing and the other decreasing with decreasing x . This would mean that B is shifted to higher temperatures probably on account of the larger variety of cations present in Mn-Cu-Fe spinels. Let us add that the two peaks reported in Ref. 22 for the case of Mg-Cu ferrites may be interpreted in the same way.

The agreement between ϵ_M and ϵ_σ is reasonable and the only qualitative difference from the Mn-Fe case may be seen in the character of the transition over the critical concentration $x = 0.5$ which is much more smeared out here. We believe that the explanation is based on a gradual change in distribution of ions and valencies so that the actual electronic states may be

⁵⁰H. J. Van Hook and M. L. Keith, Amer. Min. ral. **43**, 69 (1958).

quite complicated. In spite of this the main features of the transport processes in Mn-Fe spinels seem to be retained also in Mn-Fe-Cu system. On the other hand the effect A cannot be found down to 2°K. This may be connected with the absence of single-ion anisotropy for Cu^{2+} .

V. CONCLUSION

Information obtained from experimental and theoretical studies of induced anisotropy and various types of aftereffect concerns not only the nature of anisotropic interactions of different arrangements and the mechanism of their attaining equilibrium but also more general aspects of crystal equilibria. As an example, our results on magnetic loss spectra of Mn-Fe ferrites in the temperature range from 2° to 360°K were described in detail and an interpretation suggested. The latter is based on the known data concerning the cation and valency distribution in the manganese ferrosinels studied, and the temperature behavior of magnetic relaxation was compared with the electrical properties measured earlier. Three relaxation processes differing in the temperature ranges of the corresponding $\tan\delta$ maxima were identified and ascribed successively with rising temperature to reorientation of Jahn-Teller distortion of unstabilized Mn^{3+} octahedra, ordering of Fe^{2+} ions by means of electron transfer, and to reorientations of Jahn-Teller distortions of Mn^{3+} ions stabilized by means of electrons. A similar study performed for the $\text{Cu}_{0.5}\text{Mn}_x\text{Fe}_{2.5-x}\text{O}_4$ system showed that the relaxation processes and electrical conductivity displayed a similar transition between iron-rich and iron-deficient compositions, but less sharply defined than in the case of $\text{Mn}_x\text{Fe}_{3-x}\text{O}_4$ system.

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