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Analogy between the effects of low-energy-ion and fast-neutron bombardments on the garnet structure

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An analogy between the effects of low-energy-ion and fast-neutron bombardments on the garnet structure is established from the changes observed in the magnetic properties (magnetization, Curie temperature) and the crystalline properties (lattice parameter, amorphization) of bombarded garnets. The nature of the induced damage is examined by the assumption of a transformation of Fe^{3+} ions into Fe^{2+} ions in tetrahedral sites.

I. INTRODUCTION

During the last ten years, many experimental results have been published on the physical properties of garnets bombarded by various kinds of particles: electrons, fast neutrons, thermal neutrons, low-energy ions, and high-energy heavy ions. The essential mechanisms of particle-crystal interactions leading to structural changes are elastic nuclear collisions, electronic collisions, and nuclear reactions. They produce displacements of electrons and ions in the crystal.

The case of garnets bombarded by low-energy ions is of great interest since Wolfe *et al.*[1] discovered in 1971 that the properties of bubble garnets could be improved by ion implantation. Since then, the magnetic and crystallographic properties of ion-bombarded garnets have been much studied (see, for example, Ref. 2). However, the mechanism of the ionic structure transformation which is responsible for the changes in their physical properties is not known at present.

In this paper we propose a new approach to investigate these mechanisms, based on the fact that the particle-crystal interaction in both low-energy-ion bombardment[3,4] and fast-neutron irradiation[5] is governed by the same mechanism of elastic nuclear collisions. We then compare the effects of low-energy-ion and fast-neutron bombardments by referring to experimental results published in the literature.

II. COMPARISON OF EFFECTS OF LOW-ENERGY-ION AND FAST-NEUTRON BOMBARDMENTS

Let us examine the variations of lattice volume $\Delta V/V$, magnetization $\Delta(4\pi M)$, Curie temperature ΔT_C, and the crystallographic phase induced by low-energy-ion and fast-neutron bombardments. We consider only rare-earth iron garnets with small Ge or Ga concentrations, x, for $0 \leq x < 1$ where the Néel model is applicable.[6,7]

For fast-neutron irradiated polycrystals the lattice volume variation $\Delta V/V$ is defined as $\Delta V/V = 3\Delta a/a$, Δa being the increase in the lattice constant. For ion-implanted single crystals, $\Delta V/V$ is defined as $\Delta V/V = \Delta a/a$, where Δa is the increase in the lattice constant perpendicular to the surface, the sample being free to expand only in this direction.

For a quantitative analysis of $\Delta(4\pi M)$ and ΔT_C as a function of $\Delta V/V$, the following bombardment conditions may be chosen: (a) low doses of particles N and low particle flux leading to relatively small volume variations such as, $0 \lesssim \Delta V/V \lesssim 1.5\%$, the main part of the bombarded crystal remaining crystalline; and (b) energy and mass of bombarding ions chosen such that the transformed crystal has a thickness $d \gtrsim 1000$ Å.

A. Correlation between the changes in magnetization and lattice volume

We have shown in Fig. 1 the variation at room temperature of lattice volume $\Delta V/V$ and magnetization $\Delta(4\pi M)$ with the dose of particles N in garnets bombarded with Ne^+ ions, $H_2{}^+$ ions, and fast neutrons, respectively.

The results with Ne^+ ions and $H_2{}^+$ ions were obtained by Speriosu and Wilts[8] in a gallium iron garnet ($x_{Ga} \approx 0.4$) under the following conditions: Ne^+ ion energy $E_n \approx 190$ keV, $H_2{}^+$ ion energy $E_n \approx 120$ keV, low current density $i \approx 0.25$ $\mu A/cm^2$, and temperature ≈ 300 K. The results with fast neutrons were obtained by Podsekin, Sarin, and Zaitsev[9,10] in an yttrium iron garnet under the following conditions: neutron energy $E_n \geq 0.1$ MeV, low neutron flux density $\phi_t \approx 1.10^{13}$ $cm^{-2} sec^{-1}$, and temperature ≈ 350 K.

For both ion-implanted and fast-neutron irradiated gar-

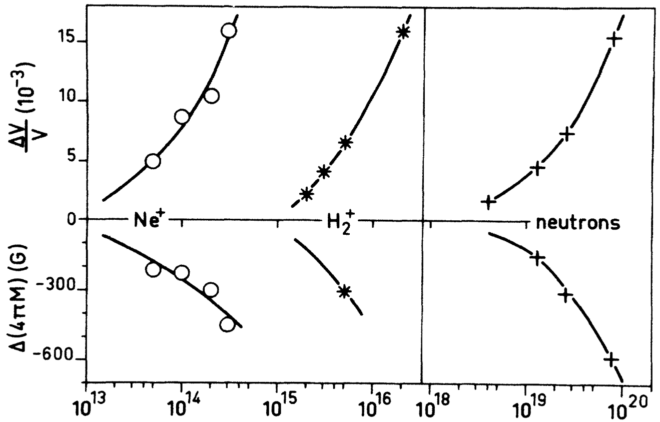

FIG. 1. Changes in lattice volume $\Delta V/V$ and in magnetization $\Delta(4\pi M)$, at room temperature, as a function of the dose of particles N, in garnets bombarded with Ne^+ ions (from Ref. 8), with H_2^+ ions (from Ref. 8), and with fast neutrons (from Refs. 9 and 10).

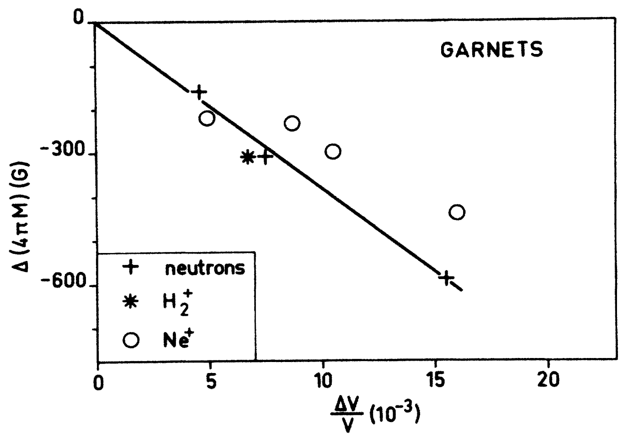

FIG. 2. Relation between the magnetization variation $\Delta(4\pi M)$ and the lattice volume variation $\Delta V/V$, at room temperature, in garnets bombarded with Ne^+ ions (from Ref. 8), with H_2^+ ions (from Ref. 8), and with fast neutrons (from Refs. 9 and 10). Continuous line: linear law corresponding to the model based on the transformation of Fe_d^{3+} into Fe_d^{2+}, deduced from Ref. 16.

nets a similar behavior is observed. There is an increase in the lattice volume, a decrease in magnetization, and the curves are of the same shape.

We have plotted in Fig. 2 $\Delta(4\pi M)$ as a function of $\Delta V/V$ (deduced from Fig. 1) for Ne^+ ions, H_2^+ ions, and fast neutrons. A striking concordance is observed in that a single linear law is obtained, which is characteristic of the garnet ionic structure after bombardment, irrespective of the nature and quantity of bombarding particles.

B. Correlation between changes in Curie temperature and lattice volume

We have shown in Fig. 3 the variation of lattice volume $\Delta V/V$ and Curie temperature ΔT_C with the dose of particles N in garnets bombarded with Ne^+ ions and fast neutrons, respectively.

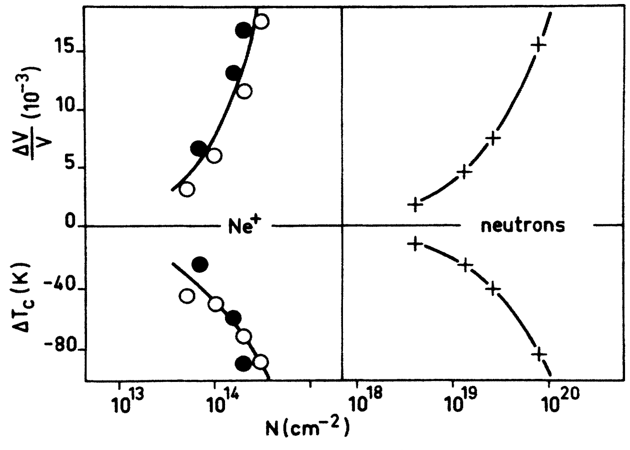

FIG. 3. Changes in lattice volume $\Delta V/V$ and in Curie temperature ΔT_C, as a function of the dose of particles N, in garnets bombarded with Ne^+ ions (open circles from Ref. 11; filled circles from Refs. 12, 13, and 14), and with fast neutrons (from Ref. 9).

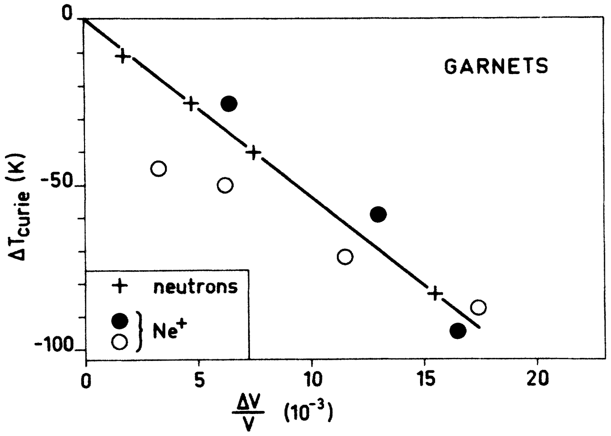

FIG. 4. Relation between the Curie temperature variation ΔT_C and the lattice volume variation $\Delta V/V$, in garnets bombarded with Ne^+ ions (open circles from Ref. 11; filled circles from Refs. 12, 13, and 14), and with fast neutrons (from Ref. 9).

The results with fast neutrons[9] were obtained under the conditions described above. The results with Ne^+ ions (open circles) were obtained by Vella-Coleiro *et al.*[11] in a germanium iron garnet ($x_{Ge} \approx 0.8$) with ion energies $E_n \approx 270$ keV. The results with Ne^+ ions (filled circles) were obtained by Komenou, Hirai, Asama, and Sakai[12] for $\Delta V/V$, and by Maartense and co-workers[13,14] for ΔT_C in a germanium iron garnet ($x_{Ge} \approx 0.9$) with ion energies $E_n \approx 100$ keV. The same behavior is observed for both ion-implanted and fast-neutron irradiated garnets.

We have plotted in Fig. 4 ΔT_C vs $\Delta V/V$ (deduced from Fig. 3) for Ne^+ ions and fast neutrons. Again, a single curve is obtained which is characteristic of the garnet ionic structure after bombardment.

The mean values of the experimental errors on $\Delta(4\pi M)$, ΔT_C and $\Delta V/V$, are approximately ±1% for fast-neutron experiments and ±10% for low-energy-ion experiments.

Considering (1) that data on neutron-irradiated garnets were obtained with bulk samples (volume ≈ 10 mm^3), while those on ion-implanted garnets were obtained with thin films (volume $= 10^{-3}$ mm^3), and (2) that the experimental results were obtained in different laboratories (U.S.A., Japan, Canada, and U.S.S.R), under different conditions of bombardment, and with different garnet samples and methods of measurement, the quantitative agreement between data on neutron-irradiated and ion-implanted garnets in Figs. 2 and 4 is remarkable.

C. Crystalline phase transformation

It is known that magnetic bubble garnets implanted with ions at very high doses are in an amorphous state. At low doses, the lattice constant increases linearly with the dose and the structure remains crystalline. At high doses, two phases are observed: a crystalline and an amorphous one. At very high doses the whole crystal becomes amorphous: Just before total amorphization, the lattice volume of the crystalline part increases up to a limit value $(\Delta V/V)_L$ of the order of 3%,[8] irrespective of the bombarding particles (Table I).

Recently, the same behavior was reported for fast-neu-

TABLE I. Limit value of the garnet-lattice-volume increase induced by particle bombardment.

Bombarding particles	Limits $\left\|\frac{\Delta V}{V}\right\|$ (%)
H_2^+ (Ref. 8)	3.9
He^+ (Ref. 8)	3.4
Ne^+ (Ref. 8)	2.5
Fast neutrons (Ref. 15)	2.4

tron irradiated garnets. When using a high fast-neutron flux $\phi_f \approx 10\times10^{13}$ $cm^{-2}sec^{-1}$, Chukalkin, Shtirts, and Goshchitskii[15] observed that $Y_3Fe_5O_{12}$ became progressively amorphized and found, when the complete amorphous state was reached $(\Delta V/V)_L \approx 2.4\%$ (Table I).

III. DISCUSSION ON THE BUBBLE-GARNET-IONIC STRUCTURE TRANSFORMATION INDUCED BY LOW-ENERGY-ION BOMBARDMENT

The analogy between the effects of low-energy-ion and fast-neutron bombardment on the garnet physical properties established above suggests that the induced ionic structure transformation is the same.

In the case of fast-neutron irradiated $Y_3Fe_5O_{12}$ the properties of the crystalline phase are well interpreted by the model based on the transformation of Fe_d^{3+} ions into Fe_d^{2+}.[16] The main consequences of this transformation are (1) a change in magnetization corresponding to a decrease in the magnetic moment of the tetrahedral iron cations from $5\mu_B$ to $4\mu_B$, (2) an increase in the lattice volume due to the ion size effect of the Fe^{2+} cation in the tetrahedral site, and (3) a decrease in Curie temperature due to a weakening of the superexchange interaction energy of the new linkages $Fe_d^{2+}-O^2-Fe_a^{3+}$ and $Fe_d^{2+}-O^--Fe_a^{3+}$.

This model assumes that (a) the iron cations remain in their initial position, and (b) the oxygen anions can move to the nearest empty interstitial space under the action of elastic nuclear collisions.

The linear law between the changes in magnetization $\Delta(4\pi M)$ and lattice volume $(\Delta V/V)$, which can be deduced from this model, is experimentally observed for both fast-neutron and low-energy-ion bombarded garnets (Fig. 2).

This correlation strongly suggests that the main damage can be the transformation of Fe_d^{3+} into Fe_d^{2+}. Does there exist direct experimental evidence for the presence of Fe^{2+} ions? Let us examine the behavior of ion-implanted bubble garnets in four other fields: the Mössbauer effect, optical absorption, annealing treatment, and ferromagnetic resonance.

A. Mössbauer effect

The effects of H^+ proton bombardment on the crystallographic properties of $Y_3Fe_5O_{12}$ were reported by Marest *et al.*[17] Measurements were performed by use of the conversion electron Mössbauer spectroscopy. After H^+ bombardment, the spectra of $Y_3Fe_5O_{12}$ showed two new features: (a) a new magnetic component, previously observed by Morrish, Picone, and Saegusa,[18] and (b) an increase in the linewidth.

The authors explained these results by the presence of a new (d') site having a hyperfine field a little weaker than the (d) site. The sum of the contributions of (d) and (d') sites corresponds to the total tetrahedral (d) site intensity of $Y_3Fe_5O_{12}$ before bombardment. Consequently, this (d') component is unambiguously due to a modification of part of the tetrahedral (d) sites. The increase in the linewidth might be explained by a possible variation of the iron valence state.

These results show clearly that H^+ bombardment of $Y_3Fe_5O_{12}$ modifies a part of the tetrahedral sites, as expected from the transformation of Fe_d^{3+} into Fe_d^{2+} in tetrahedral sites.

B. Optical absorption

Hansen, Tolksdorf, and Schuldt[19] observed that in substituted $Y_3Fe_5O_{12}$ garnets in which Fe^{2+} ions replaced Fe^{3+}, the optical absorption coefficient was proportional to the Fe^{2+} concentration. Seman, Wemple, and North[20] reported the effects of H^+ proton bombardment on the optical absorption of garnets. After bombardment, the spectra showed a linear relationship betwen the excess absorption magnitude and the H^+ proton dose.

The authors showed that the excess absorption was an absorption tail on $O(2p) \rightarrow Fe(3d)$ charge-transfer bands. A change of the valence state from Fe^{3+} to Fe^{2+} was assumed to be a contributing factor to the excess optical absorption. The linear relationship between the optical absorption coefficient and the H^+ proton dose is similar to the law obtained by replacing Fe^{3+} ions by Fe^{2+} ions in substituted garnets.[19]

C. Annealing treatment

It is known that the radiation damage in ion-implanted garnets is annealed in two stages.[2] The first stage corresponds to a temperature of 600 °C at which the crystal completely recovers its magnetization,[8] and the second stage corresponds to a temperature of around 1000 °C at which the crystal recovers its initial crystalline state.[11] The first stage (600 °C) is consistent with the change of valence $Fe^{2+}-Fe^{3+}$ (charge transfer), the second stage (1000 °C) with the displacement of oxygen anions (ion migration).

D. Ferromagnetic resonance

The low-temperature dependence of the ferromagnetic resonance linewidth of garnets is very sensitive to the presence of Fe^{2+}. In substituted $Y_3Fe_5O_{12}$ garnets, in which Fe^{2+} ions replaced Fe^{3+}, Hansen, Tolksdorf, and Schuldt[19] observed a maximum linewidth at about 40 K corresponding to a valence-exchange Fe^{2+}-Fe^{3+} relaxation mechanism (in agreement with the result of Spencer, Lecraw, and Linares, Jr.[21] and Hartwick and Smit[22]).

In the case of high-energy, heavy-ion-bombarded garnets, a direct experimental evidence for the presence of Fe^{2+} has been found by Heitman, Hansen, and Spohr.[23] The temperature dependence of the linewidth of Xe^+ ions bombarding $Y_3Fe_5O_{12}$ exhibits a remarkable maximum at 40 K attributed to Fe^{2+} centers.

The comparison between the two cases of high-energy ion and low-energy ion is probably valid since the crystalline part between the amorphous nuclear tracks shows the same correlation between the changes in Curie temperature and in lattice volume. For a Xe^+-ion dose of 10^{11} cm^{-2}, $\Delta T_C = -6$ K (Ref. 23) and $\Delta V/V = 1\times 10^{-3}$ (Ref. 24) in agreement with the slope of $\Delta T_C = f(\Delta V/V)$ in Fig. 4: $\Delta T_C = -5.5$ K for $\Delta V/V = 1\times 10^{-3}$.

IV. CONCLUSION

An analogy between the effects of low-energy-ion and fast-neutron bombardments on the garnet structure is established from the changes observed in magnetic (magnetization, Curie temperature) and crystalline (lattice parameter, amorphization) properties in accordance with the fact that the mechanism of elastic nuclear collisions is predominant in these two cases.

The changes in several physical properties of bubble garnets after low-energy-ion bombardment can be interpreted coherently by the assumption of a transformation of $Fe_d{}^{3+}$ ions into $Fe_d{}^{2+}$ ions. However, further studies such as those of the ferromagnetic resonance at low temperature and the electrical conductivity after ion implantation seem to be necessary for establishing conclusively the existence of Fe^{2+}.

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