Anomalous manifestation of long-lived photoinduced dichroism in $NaCa_2Mn_2V_3O_{12}$ garnet

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In the garnet $NaCa_2Mn_2V_3O_{12}$, a sharp dependence of photoinduced absorption, ΔK, on the pumping light polarization was observed: the ratio between the maximum and minimum values of ΔK exceeds 10. This ratio, characterizing optical dichroism, is much less (1.1–1.2) for the garnets $Ca_3Mn_2Ge_3O_{12}$ and $Ca_3Ga_{1.99}Mn_{0.01}Ge_3O_{12}$ where the dichroism, created by a polarized pumping light, relaxes *slower* after switching off irradiation. Hence, the degree of dichroism is mainly determined on the stage of its creation. Based on this and other experimental facts, a microscopic mechanism of dichroism is proposed and grounded; it involves a two-site anisotropic structure of holes photoproduced in the oxygen sublattice of a garnet.

I. INTRODUCTION

Long-lived photoinduced phenomena in magnetic insulators were observed by many research groups (e.g., Refs. 1–14) and associated with the photoinduced transfer of charges. In ferromagnets or ferrimagnets, whose Curie temperature exceeds the upper temperature boundary of the existence of long-lived photoinduced phenomena, interrelated photoinduced changes in optical and magnetic properties make up a complicated entangled picture (e.g., the illumination of the yttrium iron garnet $Y_3Fe_5O_{12}$ with linearly polarized light affects magnetic anisotropy,[1–3] domain structure,[4] and optical dichroism.[3])

To separate photoinduced changes of optical properties from those of magnetic characteristics, the authors[12–14] recently examined the antiferromagnetic garnet $Ca_3Mn_2Ge_3O_{12}$ in a broad temperature region above the Neel temperature $T_N = 13.85$ K as well as the paramagnetic garnets $Ca_3Ga_{2−x}Mn_xGe_3O_{12}$ with $x = 0.01, 0.02$ (long-lived photoinduced changes are observed up to about 270 K). In the absence of magnetic ordering, photoinduced optical phenomena in the mentioned set of garnets have common well-pronounced features, which enabled us to elucidate the physical picture.[12–14] Photoinduced optical phenomena comprise photoinduced absorption $\Delta K = K(I) − K(0)$, where $K(I)$ is absorption coefficient under pumping with intensity I, and dichroism. Dichroism is measured by the difference, $\Delta K_{max} − \Delta K_{min}$, between the maximum and minimum of the quantity ΔK as a function of the pumping polarization direction, the probe light polarization being fixed.

For the examined garnets $Ca_3Mn_2Ge_3O_{12}$ and $Ca_3Ga_{2−x}Mn_xGe_3O_{12}$ with $x = 0.01, 0.02$, the relaxation kinetics of photoinduced absorption and dichroism, observed after switching off irradiation, is of a similar character. The relaxation curve is a superposition of a continuous set of decay components with decay time varying in a range from a minute to many hours (a special analysis proves that decay times fill in continuously this interval.[14]) As temperature rises, the observed decay kinetics do not noticeably change while ΔK diminishes by an order of magnitude. Such decay kinetics cannot be ascribed to some new irradiation-produced optical centers but is naturally explained by random electric fields of photoproduced localized charges (holes). These fields play a dual role: they enhance the optical transition observed and strongly promote delocalization of holes, thus accelerating their recombination. A broad continuous set of decay times is conditioned by a continuous distribution of random electric fields over magnitude. Such notion was quantitatively corroborated by the solution of the corresponding kinetic equation with realistic values of parameters.[12,13]

Photoinduced dichroism, observed in the garnets $Ca_3Mn_2Ge_3O_{12}$ and $Ca_3Ga_{2−x}Mn_xGe_3O_{12}$ simultaneously with photoinduced absorption ΔK, has the same relaxation kinetics but is significantly weaker (when varying the polarization direction, the difference $\Delta K_{max} − \Delta K_{min}$ amounts to 10–20%).[13,14]

But in the garnet of a related composition $NaCa_2Mn_2V_3O_{12}$, examined in the present work, dichroism is found to be anomalously strong: the difference $\Delta K_{max} − \Delta K_{min}$ exceeds 90% of ΔK_{max}. This fact, in combination with the relaxation kinetics observed, gives a clue to elucidating the nature of photoinduced dichroism in the garnets of the considered class.

II. EXPERIMENT

The samples of the single crystal $NaCa_2Mn_2V_3O_{12}$ were cut in the form of 25–50 μm thick plane-parallel plates perpendicular to the [100] direction. Photoinduced phenomena were examined with an optical double-beam setup. The sample was illuminated by a He-Ne laser ($\lambda = 633$ nm, flux density of 0.13 W/cm^2). A stable wide-band emission of an arc xenon lamp, dispersed through a monochromator, served as probe light with $\lambda = 590$ nm. The intensity of the probe beam was low enough to cause no photoinduced phenomena.
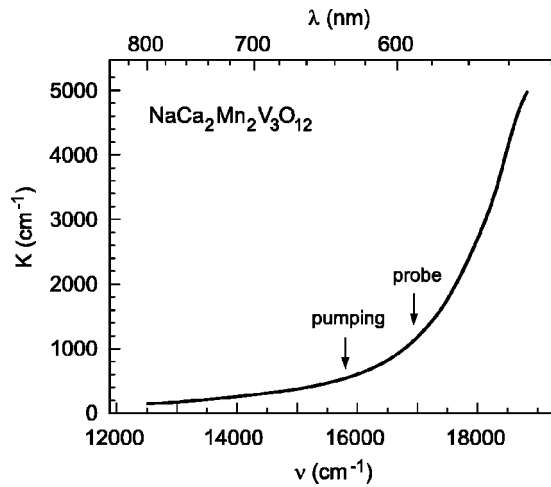
FIG. 1. Absorption spectrum of the garnet $NaCa_2Mn_2V_3O_{12}$ at 30 K. The frequencies of the pumping and probe light are shown by arrows.

After passing through the sample, the probe beam was run through a second monochromator tuned to the probe light wavelength in order to cut off the scattered pumping light. The initial absorption spectrum measured is shown in Fig. 1.

To examine photoinduced dichroism, probe light was polarized in the lattice direction [110] and photoinduced absorption was measured under irradiation with light polarized parallel ($\Delta K_{\parallel} \equiv \Delta K_{min}$) and perpendicular ($\Delta K_{\perp} \equiv \Delta K_{max}$) to the probe light polarization. In more detail, the optical setup was described in Ref. 13.

Figure 2 demonstrates the measured dichroism and its kinetics under changing conditions of pumping. At first, photoinduced absorption ΔK was measured under unpolarized pumping that at $t=10$ min was changed to the pumping polarized perpendicularly to the probe light polarization. As a result, ΔK took on an almost twice greater value $\Delta K_{\perp}$. Then, at $t=15$ min, the pumping polarization direction was switched parallel to the probe light polarization, causing the
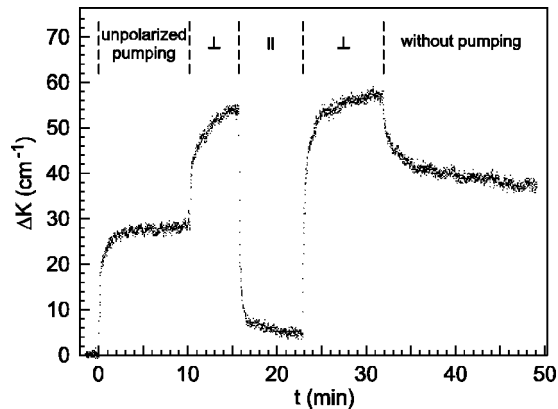

FIG. 2. Time dependence of photoinduced absorption ΔK at 30 K under pumping conditions sequentially changed as indicated in the figure. The sample was irradiated at first with unpolarized light and then with light polarized in turn perpendicular ($\perp$) and parallel ($\parallel$) to the probe light polarization. Relaxation after switching off irradiation is also shown.
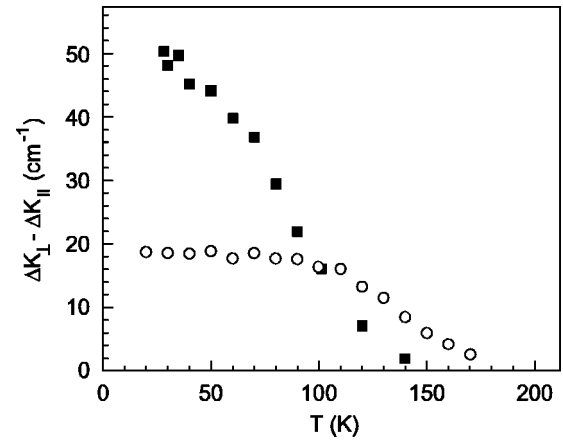

FIG. 3. Temperature dependence of the photoinduced dichroism $\Delta K_{\perp} - \Delta K_{\parallel}$ for $NaCa_2Mn_2V_3O_{12}$ (squares). For comparison, the corresponding dependence is shown for $Ca_3Mn_2Ge_3O_{12}$ by circles.

diminution of ΔK down to a small value $\Delta K_{\parallel} \approx 0.1 \Delta K_{\perp}$; this indicates on a high relative degree of dichroism $\Delta K_{\perp} / \Delta K_{\parallel} \approx 10$. After switching (at $t=23$ min) to the perpendicular polarization, ΔK grew ten times. At $t=32$ min pumping was switched off, and ΔK began to diminish (first very fast and then much slower) in the course of relaxation.

Let us define the mean relaxation rate as

$$R_{relax} = [\Delta K(0) - \Delta K(20\ min)]/\Delta K(0), \qquad (1)$$

where time is counted from switching off irradiation. Figure 2 gives $R_{relax} \approx 0.35$ for $NaCa_2Mn_2V_3O_{12}$. For $Ca_3Mn_2Ge_3O_{12}$, the corresponding value of 0.12 (Ref. 13) indicates on a considerably slower relaxation.

Figure 3 shows the temperature dependence of dichroism $\Delta K_{\perp} - \Delta K_{\parallel}$ under irradiation lasting long enough that $\Delta K_{\perp}$ and $\Delta K_{\parallel}$ become independent of time. For comparison, the temperature dependence of the same quantity for $Ca_3Mn_2Ge_3O_{12}$ is plotted by circles. Figure 3 demonstrates a significantly stronger temperature dependence of dichroism for $NaCa_2Mn_2V_3O_{12}$ in the region $T < 100$ K.

III. NATURE OF PHOTOINDUCED DICHROISM

The relaxation kinetics after switching off irradiation (Fig. 2) demonstrates a very long time of the complete relaxation of photoinduced phenomena (a similar relaxation kinetics was observed for $Ca_3Mn_2Ge_3O_{12}$ and $Ca_3Ga_{2-x}Mn_xGe_3O_{12}$).[12–14] This indicates that photoproduced charges are very heavy holes with a long time of recombination.

In the garnets $NaCa_2Mn_2V_3O_{12}$, $Ca_3Mn_2Ge_3O_{12}$,[12,13] and $Ca_3Ga_{2-x}Mn_xGe_3O_{12}$ (Ref. 14) photoinduced absorption can be excited by red light with photon energy (of about 2 eV) much less than the ionization energy of any lattice cation (>30 eV) but comparable with the electron affinity of oxygen ions. Hence, pumping creates holes (O^- ions) in the sublattice of oxygen ions O^{2-} with the closed-shell configuration of Ne.

On the other hand, a many-hour lifetime of photoproduced oxygen holes (see Fig. 2) indicates that they exist in

TABLE I. The ratio of the valence p-state radius ρ to the corresponding interatomic distance b.

| Crystal	ρ/b	$\rho(\text{Å})$	$b(\text{Å})$
$Ca_3Ga_2Ge_3O_{12}$	0.293	1.54	5.25
Ne	0.166	0.99	5.97
Ar	0.245	1.74	7.10
KCl	0.193	1.62	8.40
KI	0.250	2.36	9.42
NaI	0.273	2.36	8.63

FIG. 4. Origin of photoinduced dichroism: a two-site oxygen hole (quasimolecule), got into the first coordination sphere of the ion A, creates electric field perpendicular to the quasimolecule axis and to the pumping polarization direction.

the form of tight-bound polarons, whereas the existence of a sharp long-lived dichroism in $NaCa_2Mn_2V_3O_{12}$ evidences that these polarons have a strongly anisotropic structure. Based on this, one can assume that an oxygen hole polaron in garnets exists in the form of a two-atom quasimolecule O^--O^{2-} that possesses both the earlier properties. The quasimolecule constituents, O^{2-} and O, have the configurations $1s^22s^22p^6$ and $1s^22s^22p^5$, respectively; the former is the closed-shell configuration of Ne and the latter is that with a p hole.

Such assumption is grounded by the following facts. The structure of a stable hole polaron is well known for the crystals of Ne, Ar, Kr, and Xe, consisting of atoms with a closed valence shell ns^2np^6. The valence np hole, distributed between two adjacent atoms separated by a distance r, realizes a strong exchange binding (of about 1 eV), that sharply grows with decreasing r and brings together two adjacent atoms.[15] Similar two-site holes (called V_k centers), formed in the anion sublattice of alkali halides, are also known to be stable polaronic states.[16,17] For all mentioned crystals, the exchange binding is in main determined by the ratio of the valence p-state radius ρ to the corresponding interatomic distance b in the ideal lattice. As seen from Table I, ρ/b is greater for a garnet than for other crystals where the existence of stable two-atom hole polarons has been established reliably. Hence, stable two-atom hole polarons must exist also in the O^{2-}-sublattice of garnets.

Photoinduced dichroism can be naturally explained by the anisotropy of a two-site hole polaron in the oxygen sublattice. Photoinduced absorption is associated with optical transitions in a lattice ion labeled as ion A (in $Ca_3Mn_2Ge_3O_{12}$, A=Mn^{3+};[12–14] in $NaCa_2Mn_2V_3O_{12}$, A cannot be exactly identified yet). The field of photoproduced charges, **F**, enhances this transition for the probe light polarized parallel to **F**. As seen from Fig. 4, the direction **F** is mainly perpendicular to the axis of the quasimolecule O^--O^{2-} given by the pumping polarization direction. Thus, $\Delta K_\perp > \Delta K_\parallel$ in accordance with experiment.

A drastic difference in the degree of dichroism between the garnets $NaCa_2Mn_2V_3O_{12}$ and $Ca_3Mn_2Ge_3O_{12}$ is obviously connected with a different degree of the two-site hole depolarization. However, the depolarization mechanism cannot be associated with the relaxation (recombination) of a hole after its creation. Indeed, as was mentioned in Sec. II, the $NaCa_2Mn_2V_3O_{12}$ garnet with a very strong dichroism is characterized by a greater relaxation rate R_{relax} compared to the garnet $Ca_3Mn_2Ge_3O_{12}$ with a weak dichroism (R_{relax} =0.35 and 0.12, respectively).
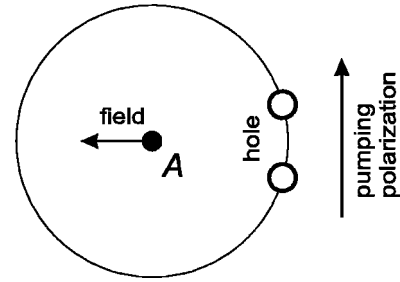
A proper mechanism of hole photoproduction, proposed in Ref. 14, involves the following subsequent processes.

(1) A lattice ion, labeled by C, is excited by pumping (ion C may be different from ion A serving as a probe center for photoinduced effects; in $Ca_3Mn_2Ge_3O_{12}$ ion C=Mn^{3+}).[12,13] The pumping, linearly polarized in the z direction, brings the ion into one of the (approximately) degenerate excited states $\langle j|$ ($j=0,1,\ldots$) with a nonzero matrix element $\langle j|z|\text{ground}\rangle$ between the excited and ground states. This excited state is labeled by $j=0$.

(2) The excitation energy, E_{exc}, of the ion C is expended for creating a pz hole in the O^{2-} sublattice, an electron being transferred from O^{2-} to the excited ion C. Such process is possible if E_{exc} exceeds the minimal energy, E_{min}, required for creating an oxygen hole. Generally, $E_{min} \sim 2$ eV (electron affinity of O^- in the lattice). At $E_{exc} > E_{min}$, the creation of an oxygen hole (a hole analog of autoionization) requires overcoming an energy barrier B that diminishes with an increase of the positive difference

$$\Delta E = E_{exc} - E_{min}. \qquad (2)$$

The lifetime, τ_{exc}, of the excited state $\langle j=0|$ relative to creating a hole is highly sensitive to the barrier B. During this lifetime, the initial excited state $\langle j=0|$ can be depolarized (i.e., turned to a state $\langle j \neq 0|$ with $\langle j|z|\text{ground}\rangle=0$) by random electric fields which break the symmetry of the lattice Hamiltonian and cause transitions between different states $\langle j|$. Thus, the probability of depolarization, mainly proportional to τ_{exc}, strongly diminishes with an increase of the difference (2).

A sharp difference in dichroism of the garnets $NaCa_2Mn_2V_3O_{12}$ and $Ca_3Mn_2Ge_3O_{12}$ with nearly coinciding E_{exc} indicates that in the former case E_{min} is lower. This becomes illustratively understandable if the ion C is identified with V^{5+} in $NaCa_2Mn_2V_3O_{12}$ and with Mn^{3+} in $Ca_3Mn_2Ge_3O_{12}$.[12,13] Since the fifth ionization potential of a free V atom (65 eV) much exceeds the electron affinity (~ 2 eV) of the six oxygen neighbors in the lattice, even in the ground state a noticeable part of oxygen electrons is transferred to the V^{5+} ion, so that a hole in O^{2-} is partially formed. The greater is the ionization potential of the cation C, the stronger such electron transfer to it from oxygen neighbors is pronounced and the lower is the excitation en-

ergy E_{min} necessary for a complete hole formation in the O^{2-} ion. In the garnet $Ca_3Mn_2Ge_3O_{12}$, where the ion $C=Mn^{3+}$ has the third ionization potential of 34 eV, the degree of electron transfer from O^{2-} to C must be significantly less and E_{min} correspondingly higher than in the case of $NaCa_2Mn_2V_3O_{12}$. Note that in both cases the ion C is excited within the charge transfer transition (an enhancement of the portion of electron transferred to C) whose energy is much lower than the energy of the excitation of a free V^{5+} ion.

(3) The oxygen pz hole, created in a free band state, rapidly covers in the O^{2-} sublattice a distance of many lattice periods without depolarization. Then the hole comes to a two-site polaronic state with axis oriented in the z direction. Its strong binding (~ 1 eV) entails a long hopping time strongly affected by random electric fields. Hopping time determines the hole lifetime relative to recombination, whereas the time of depolarization of a two-site hole is significantly larger;[17] hence, both photoinduced absorption and dichroism actually relax through recombination by a similar time law, in accordance with the experiment.[13]

Thus, to all appearance, stage 2 is responsible for a sharp difference in photoinduced dichroism between the cases of $NaCa_2Mn_2V_3O_{12}$ and $Ca_3Mn_2Ge_3O_{12}$ ($\Delta K_{max}/\Delta K_{min}=10$ and 1.2, respectively). The difference between these cases in the temperature dependences of dichroism (see Fig. 3) is explained also. Stage 1 is a pure electronic process independent of temperature. But stage 2, accompanied by overcoming an energy barrier in the lattice, has a thermally assisted character. Hence, an increase of temperature significantly shortens the time, τ_{exc}, of creating a hole, thus diminishing the depolarization of the created hole. This partly compensates the increasing temperature dependence of the recombination of hole polarons (stage 3) resulting in a weak temperature dependence of the observed dichroism in the range of not very high temperatures. In accordance with experiment (Fig. 3), such compensation takes place for $Ca_3Mn_2Ge_3O_{12}$ and not for $NaCa_2Mn_2V_3O_{12}$ in view of a negligibly weak depolarization on stage 2.

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