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Photoinduced reduction of V^{4+} ESR signal intensity in $Ca_2NaMg_2V_3O_{12}$ garnet

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Abstract. The occurrence of a photoinduced reduction of the V^{4+} ESR signal intensity in $Ca_2NaMg_2V_3O_{12}$ is reported. Its time and temperature dependences are considered and a comparison is made with the photomagnetic effects observed in $Y_3Fe_5O_{12}$. The intensity reduction is attributed to light-induced electron transport within the vanadium sublattice. In this respect the results of photoconductivity and optical reflectance measurements are also presented and discussed.

1. Introduction

The garnets form a large group of compounds with general formula $\{C_3\}[A_2](D_3)O_{12}$, where $\{C\}$, $[A]$, (D) denote ions on dodecahedral, octahedral and tetrahedral sites respectively. The sublattices may accommodate a variety of cations such as C = rare-earth ions, Y, Ca, Na, Sr; A = Fe, Al, Mg, Ni, Ga; D = Fe, Al, Si, Ge, V.

Yttrium and rare-earth iron garnets $\{RE_3\}[Fe_2](Fe_3)O_{12}$ have been studied especially extensively because of their ferrimagnetic properties. In Si-doped or partially reduced yttrium iron garnet (YIG) interesting photoinduced changes in physical properties have been observed (Metselaar 1977). These effects have been attributed to the presence of small amounts of Fe^{2+} on the Fe^{3+} sublattices.

In a previous paper the preparation and characterisation of single crystals of $\{Ca_2Na\}[Mg_2](V_3)O_{12}$ were reported (Oversluizen and Metselaar 1982). By means of a heat treatment a number of V^{4+} ions were introduced on tetrahedral sites, analogously to the Fe^{2+} centres in YIG. The V^{4+} centres were observed in optical absorption and ESR spectra. It seemed worthwhile to use these direct identification methods to investigate the possible occurrence of photoinduced effects in vanadate garnets. In this Paper photoinduced changes in the V^{4+} ESR signal intensity are reported together with the results of photoconductivity and optical reflectance measurements. Section 2 gives experimental details. In § 3 some characteristics of the ESR photosensitivity, the optical reflectance and photoconductivity spectra are presented. The results are compared and discussed in relation to the literature in § 4 and the conclusions drawn are summarised in § 5.

2. Experimental details

$\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ single crystals were obtained from PbO and V_2O_5 fluxes. Polycrystalline material was prepared by solid state reaction. The V^{4+} centres were introduced by a heat treatment at $\approx 1130^\circ\text{C}$ in air followed by an air quench to room temperature. Details concerning the preparation conditions and the ESR equipment have been published before (Oversluizen and Metselaar 1982). During the illumination experiments light emitted by a 200 W xenon lamp was focused on a dedicated T102 measurement cavity.

The photoconductivity experiments were performed in a home-made cryostat operating at a fixed temperature. For the experiments reported here a temperature of 195 K, achieved by filling the cryostat with a dry-ice/acetone mixture, was suitable. The plane-parallel polished single crystals were spring mounted in an Al_2O_3 insulated sample holder. Good electrical contact was achieved using silver-painted electrodes. Light emitted by a 450 W xenon lamp was dispersed through Bausch and Lomb high-intensity gratings and focused on the crystals in a direction perpendicular to the electric field, thus forming a mask preventing illumination of the contacts. In the visible spectral region UV filters were employed to eliminate short-wavelength stray light. The current was measured with a Cary 401 vibrating-reed electrometer. The source consisted of a set of batteries that supplied voltages 0–300 V. Currents as small as 10^{-15} A could be reliably measured.

The 45° reflectance spectra were recorded at room temperature with a Zeiss PMQ II spectrometer equipped with a RA2 reflectance unit. The optical density was measured relative to a sodium fluoride standard.

3. Results

3.1. Photosensitivity of the V^{4+} ESR signals

The V^{51} isotope with nuclear spin $I = \frac{7}{2}$ has a natural abundance of 99.76%. The V^{4+} ESR signals correspond to a $S = \frac{1}{2}$, $I = \frac{7}{2}$ centre in tetragonal symmetry. The same centre causes optical absorption at $\approx 13 \times 10^3 \text{ cm}^{-1}$ due to ${}^2\text{B}_1 \rightarrow {}^2\text{B}_2$, ${}^2\text{E}$ crystal-field transitions (Oversluizen and Metselaar 1982). It was observed that the measured ESR signal intensity decreased upon irradiation. Several features of this photoinduced effect—temperature dependence, wavelength dependence, etc—will be outlined below. The signal intensity reduction attained and the shape of the decay curve are the same for each hyperfine line and are independent of the orientation of the magnetic field. In the temperature range 77–190 K the intensity reduction decreases only slightly towards higher temperatures. Large differences in the reduction factor may exist however between different single crystals as is illustrated by figure 1, where two typical decay curves measured at 140 K are shown. The height of the derivative signal of the first low-field line $S = \frac{1}{2}$, $M_I = -\frac{7}{2}$, when the magnetic field direction is along the tetragonal axis, is recorded as a function of time. The relative starting intensities of both lines have been normalised to one. Comparison of the curves relative to one another reveals that the maximum signal intensity reduction obtainable and the shape of the recovery curve are different for the two crystals.

The difference in composition quoted in the figure caption is probably not responsible for the observed changes because even greater differences have been observed between (non-oriented) crystals grown from the same flux. Unfortunately the measurements

performed at liquid helium temperature all concerned crystals that exhibited only a small, but still reversible, effect. Using Schott-glass filters it was established that only light in the spectral region $10\text{--}15 \times 10^3 \text{ cm}^{-1}$, i.e., corresponding to the ${}^2B_1 \rightarrow {}^2B_2$, 2E crystal-field transitions, was effective. Furthermore, it should be remarked that during illumination no other ESR signal could be detected in the field range 0–10.000 G.

Figure 1. Decay curves of the V^{4+} ESR signal intensity in $Ca_2NaMg_2V_3O_{12}$ single crystals grown from V_2O_5 and PbO fluxes (see text). Full curve: $\{Ca_{1.94}Na_{0.91}Pb_{0.10}O_{0.05}\} [Mg_{1.92}O_{0.08}] (V_{2.99})O_{12}$; broken curve: $\{Ca_{2.05}Na_{0.60}Mg_{0.11}O_{0.24}\} [Mg_2] (V_{2.99})O_{12}$.

Figure 2. Photoconductivity and powder reflectance spectra of $Ca_2NaMg_2V_3O_{12}$. Full curve: after reduction; broken curve: before reduction.

3.2. Photoconductivity and reflectance spectra

In figure 2 the room-temperature reflectance spectra from $Ca_2NaMg_2V_3O_{12}$ powders are shown together with the photoconductivity results obtained at 195 K. This temperature was chosen because at 300 K the photocurrents were too small to be detected as a function of wavelength, while at 77 K only electrical polarisation effects could be measured due to the high resistance of the crystals. The resistance of the crystals at 195 K was of the order $10^{16} \Omega$. The dark currents were always at least one order of magnitude smaller than the maximum photocurrents and exhibited linear voltage characteristics. The photocurrents were proportional to the light intensity, $I \sim G^\gamma$ with $\gamma = 1$, where I is the photocurrent and G is the light intensity. Because no essential differences were observed neither between crystals grown from different fluxes nor before or after heat treatment only one curve is shown.

The plotted curve represents the current corrected for variations in the lamp intensity in quanta/wavenumber. The magnitude of the correction factor increases rapidly above $44 \times 10^3 \text{ cm}^{-1}$. The corresponding part of the photoconductivity curve, which is the product of the decreasing photocurrent and the increasing correction factor, therefore becomes proportionally uncertain (dotted curve). Deliberate illumination of the electrical contacts did not change the observed behaviour.

The reflectance spectra nicely reproduce the results previously obtained in transmission experiments on single crystals in the range $10\text{--}26 \times 10^3 \text{ cm}^{-1}$. Partial reduction of the powder causes an increased absorption in the entire spectral region and the bands, due to V^{4+} crystal-field transitions, at $\approx 13 \times 10^3 \text{ cm}^{-1}$ are re-observed. The new information obtainable from the reflectance spectra concerns the wavelength range 400–200 nm where transmittance measurements are impossible due to the high absorbance

of the crystals. The reported intrinsic absorption edge at $\approx 26 \times 10^3 \text{ cm}^{-1}$ appears to be the side of a band peaked at $\approx 29 \times 10^3 \text{ cm}^{-1}$. A second maximum is seen at $\approx 43 \times 10^3 \text{ cm}^{-1}$.

4. Discussion

Photoeffects of the type to be discussed have been observed in several magnetic compounds (Metselaar 1977). The common factor in these materials is that they always contain ions that can assume different valences. Prior to a discussion of the results obtained with the vanadate garnet the physical mechanism of these photoinduced changes will be explained on the basis of observations made on partially reduced or Si-doped $\text{Y}_3\text{Fe}_5\text{O}_{12}$. Charge compensation in this material occurs by Fe^{2+} centres and the electrical transport properties are described in terms of thermally activated hopping of electrons between Fe ions. An electron transport from an Fe^{2+} ion to an arbitrary Fe^{3+} ion in the lattice is equivalent to a displacement of the Fe^{2+} ion to that site. If the two positions of the ferrous ion are inequivalent with respect to the physical property considered, the necessary conditions for the occurrence of photoinduced changes are met. Photoinduced transitions of electrons between cations on different lattice sites resulting in a redistribution of centres are the origin of the photoinduced changes. If the temperature is sufficiently low the change may be persistent due to the low mobility of the electrons, while at higher temperature competition occurs between photoinduced transitions and thermal electron motion. In the case of YIG many of the photoinduced changes concern the magnetic properties and have been observed both in single crystals and in polycrystalline samples. Large differences have been reported with regard to the time scale and the temperature at which the experiments were performed.

While changes in the magnetic permeability were persistent at 77 K changes in the ferromagnetic resonance frequency were reversible at 4.2 K (Enz *et al* 1969, Teale *et al* 1970). Therefore the kinetics of the photoinduced effect can only be described assuming a wide distribution of relaxation times (Crevecoeur 1969). This can be explained if the position of the energy levels of the Fe^{2+} ions varies with the distance between the electron-donating centre and the ferrous ion concerned (Enz *et al* 1971). Recent investigations of Dedukh *et al* (1980) also confirm that the garnet contains an inhomogeneous system of electron centres whose state can be altered by various types of electromagnetic radiation. In the following the photoinduced intensity reduction of the V^{4+} ESR signal will be discussed. Although several questions regarding the detailed mechanism have to remain unanswered certain similarities with the photoinduced changes encountered in YIG are obvious. Firstly, the effect observed must involve electron transport through the lattice because relaxations within the V^{4+} centre with a decay time of the order of minutes are physically unreasonable. Secondly, the differences observed between samples from the same batch, in which no differences in composition were detected, must be due to the quenching procedure or be related to natural variables in flux-grown crystals such as dislocation density. The quenching procedure was not standardised. The crystals were removed from the furnace and allowed to cool in air. In this way the temperature interval 1130–20 °C was bridged in a few minutes. Recently performed conductivity experiments (to be published) have revealed that V^{4+} centres are also formed by annealing the samples at low oxygen partial pressures at 700 °C. The measured activation energies appeared to be a function of both the concentration of V^{4+} centres and the thermal history of the samples. It is thus evident that for crystals differing in size

and geometry the above quenching procedure will result in variations in the concentration of V^{4+} centres and the distribution of vacancies. For practical reasons the ESR experiments have been performed in a single cavity without a DPPH intensity standard. The calculated intensities for different samples in that case are only a rough indication of the relative concentrations of centres. A correlation between the estimated concentrations and the magnitude of the photoinduced intensity reduction was not found. It is concluded that the $Ca_2NaMg_2V_3O_{12}$ single crystals contain an inhomogeneous system of V^{4+} centres where concentration and distribution play a major role in the occurrence of the photoinduced intensity reduction. This conclusion is further substantiated by the inhomogeneous broadening of resonance lines that was first observed and thoroughly studied by Havlicek and Novak (1974) and reproduced in our experiments. They suggested the source of this inhomogeneity to be the random distribution of Ca and Na ions over the dodecahedral sublattice. The above results indicate, however, that such a distribution alone cannot account for the observed behaviour and concentration-dependent terms must be invoked in the description of the system. To account for the fact that during illumination no other ESR signal is detected two explanations will be considered. The electrons responsible for the intensity reduction are either moving too fast to be detected or are trapped in a diamagnetic state. Bipolaron formation is a well established phenomenon in various vanadium oxides (Kawakubo *et al* 1971, Chakraverty *et al* 1978, Takahashi and Nagasawa 1981). However, there are two reasons for rejecting this mechanism in the present case. In the first place an electron-electron coupling of this kind may be expected to be strongly dependent on the distance between nearest vanadium ions. In the garnet this distance is far greater ($\approx 3.8 \text{ \AA}$) than in the vanadium oxides ($\approx 2.9 \text{ \AA}$). The second reason is the observed behaviour of the effect with temperature: a certain stabilisation energy has to be associated with the formation of bipolarons which is either large, so that the changes can be frozen in, or sufficiently small to result in a strong temperature dependence, neither of which occurs. Therefore the following process is assumed to represent best the actual situation: the energy absorbed in the crystal-field transition is sufficient to detach the electron from the vanadium ion concerned and subsequently it wanders through the lattice at a rate high compared with the ESR resonant frequency until a vanadium situated suitable for retrapping is encountered. Such a process is in agreement with the reversibility of the photoinduced changes observed. It does not explain however the fact that the decay time is nearly independent of temperature. It is not clear at present how crystal-field transitions can induce electron transport but in case of $CdCr_2S_4$ and YIG such transport has been ascertained by the observation of photocurrents after excitation in the crystal-field levels of chromium and iron respectively (Larsen and Wittekoek 1972, Suryanarayanan and Krishnan 1974).

The photoconductivity experiments reported here failed to provide a definite proof of the electron transport initiated by excitation in the V^{4+} crystal-field transitions.

Instead small photocurrents $\sim 10^{-13} \text{ A}$ were detected under illumination at wave-numbers $> 35 \times 10^3 \text{ cm}^{-1}$ in the intrinsic part of the spectrum. There is ample evidence that the absorption in the region $25\text{--}50 \times 10^3 \text{ cm}^{-1}$ must be attributed to the vanadate groups in the lattice. Blasse and Bril (1967) have studied the fluorescence of Eu^{3+} -activated $Ca_2NaMg_2V_3O_{12}$ where excitation in the vanadate groups is followed by energy transfer to the Eu^{3+} ion and subsequent emission of the characteristic Eu^{3+} spectrum. The excitation spectrum consisted of a broad band ranging from $25\text{--}50 \times 10^3 \text{ cm}^{-1}$ with a maximum at $\sim 29 \times 10^3 \text{ cm}^{-1}$. In the reflectance spectrum reported here two maxima occur at 29 and $43 \times 10^3 \text{ cm}^{-1}$. The absorption spectrum of V_2O_5 also contains two maxima about $12 \times 10^3 \text{ cm}^{-1}$ apart at 25 and $37 \times 10^3 \text{ cm}^{-1}$ (Conlon and Doyle 1961),

while in CaO and MgO absorption starts at energies $> 50 \times 10^3 \text{ cm}^{-1}$ (Neeley and Kemp 1963). In agreement with the relative magnitudes of the V–O distances, $\approx 1.6 \text{ \AA}$ in V_2O_5 and $\approx 1.9 \text{ \AA}$ in the garnet, the bands are shifted to higher energies. Since no photoconductivity is observed in the region below $35 \times 10^3 \text{ cm}^{-1}$ the absorption peaked at $\approx 29 \times 10^3 \text{ cm}^{-1}$ is attributed to transitions from the oxygen 2p band to the vanadium 3d levels. The localised character of these levels is sustained by the above ESR results. Absorption at wavenumbers $> 35 \times 10^3 \text{ cm}^{-1}$ is due to electron transfer from the oxygen 2p band to the relatively broad vanadium 4s band.

The dependence of the photocurrent on the light intensity has been calculated for some simple model systems (Bube 1960). Considering an insulator, where $I_{\text{photo}} \gg I_{\text{dark}}$ as for $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$, a linear dependence of the photocurrent on the light intensity is found in the case of one-carrier transport in the presence of traps. Such a model agrees well with the inhomogeneity of the system indicated by the ESR experiments.

5. Conclusions

When reduced $\text{Ca}_2\text{NaMg}_2\text{V}_3\text{O}_{12}$ is irradiated in the absorption bands due to the V^{4+} crystal-field transitions photoinduced changes in the V^{4+} ESR signal occur. These changes are analogous to photomagnetic effects in $\text{Y}_3\text{Fe}_5\text{O}_{12}$.

Excitation in the oxygen-2p–vanadium-4s charge-transfer band produces a small photocurrent. Its dependence on the light intensity may be described by a one-carrier insulator model with traps.

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