Nonlinear optical spectroscopy of electronic states in the yttrium iron garnet $Y_3Fe_5O_{12}$

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The two-photon absorption spectra of $Y_3Fe_5O_{12}$ have been studied for the first time. The results show that real intermediate electron states may play an important role in the formation of the nonlinear spectra of magnetodielectrics. An accurate value is found for the band gap between the $2p$ valence band and the $3d$ conduction band.

Although the structure of the electron states of magnetically ordered dielectrics has been the subject of intense experimental and theoretical research for a long time, many fundamental questions have not yet been answered unambiguously.[1,2] Among these questions are such questions as the size of the energy gap between the valence band and the conduction band, the structure of the edge bands, the nature of the corresponding optical transitions, the energy positions of the d states, and the mechanisms for transitions between them. The situation is even more complicated in the case of crystals in which the magnetic ions can be in nonequivalent sublattices. Resolving these questions may be of assistance in applying new experimental methods to magnetic dielectrics. In the present letter we report a study of the electron states in the model ferrimagnet $Y_3Fe_5O_{12}$ (YIG), carried out by the method of two-photon spectroscopy.

In this method,[3] one studies the spectrum of the "additional" absorption (ΔI) of light at the time at which a laser light pulse I_l passes through the crystal. Two-photon

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transitions are distinguished from one-photon transitions in having more-complicated selection rules; as a result, it becomes possible to extract fundamentally new information on electron states. The method of two-photon spectroscopy is being used to study semiconductors[3] and transparent dielectric crystals,[4] but it has not been used for magnetically ordered dielectrics, which usually have a low transmission because of transitions between an unfilled d shell in the band gap.

The apparatus used in the present experiments is described in Ref. 4. It uses a pulsed laser with a photon energy $\hbar\omega_l = 1.17$ and a xenon flashlamp. The spectral range of the apparatus is 2.5–4.5 eV. The high sensitivity of our apparatus [$(1\text{–}2)\times 10^{-7}$ cm/MW] and the small error ($\sim 2\%$) have made it possible to study two-photon absorption in very thin YIG samples for the first time.

Figure 1 shows the results of a study of two-photon absorption in a single-crystal YIG plate 32 μm thick, parallel to the (100) plane. The spectrum of the two-photon absorption begins at 2.5 eV and increases in a nonmonotonic way to a value $\beta = 0.3$ cm/MW at an energy of 3.51 eV. At higher energy we observe a strong absorption of the probe light. At room temperature the spectrum of the two-photon absorption consists of three regions with well-defined inflection points at energies of 2.66, 2.80, and 3.14 eV. The absolute values of β are about an order of magnitude larger than those which are usually observed in the case of direct interband transitions for materials with similar band gaps (e.g., CdS and ZnSe; Ref. 5).

Also unusual is the pronounced (~ 13-fold) decrease in the absolute values of β at equivalent points as the temperature is lowered from room temperature to 110 K;

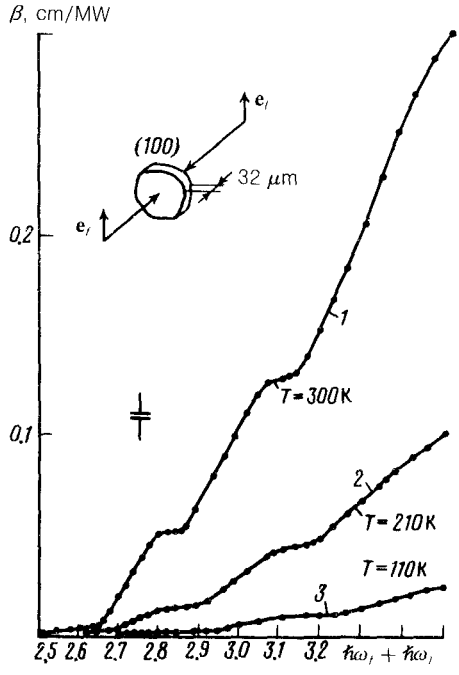

FIG. 1. Spectra of the two-photon absorption β at several temperatures: 1—298 K; 2—210 K; 3—110 K. The inset shows the polarization configuration of the experiment. Here $\mathbf{e}_l$ is the polarization unit vector of the laser beam, and $\mathbf{e}_{l'}$ is the polarization unit vector of the light from the flashlamp.

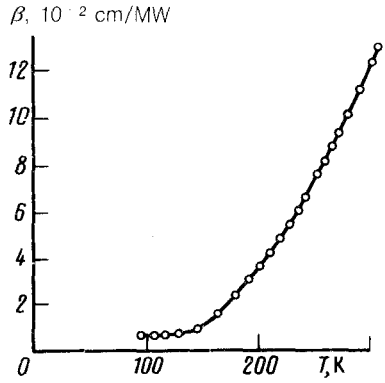

Fig. 2. Temperature dependence of β for the energy $(\hbar\omega_l + \hbar\omega_f) = 3.107$ eV.

furthermore, this pronounced decrease occurs uniformly over the entire spectrum (Fig. 1). The temperature dependence of $\beta(\hbar\omega_l + \hbar\omega_f = 3.107$ eV) is shown in Fig. 2. As the temperature is lowered to 140 K, the coefficient β decreases monotonically, while over the temperature interval from 140 to 90 K, it remains essentially constant. The latter behavior is typical of direct two-photon transitions.

To determine the mechanism for such an unusual temperature dependence of the

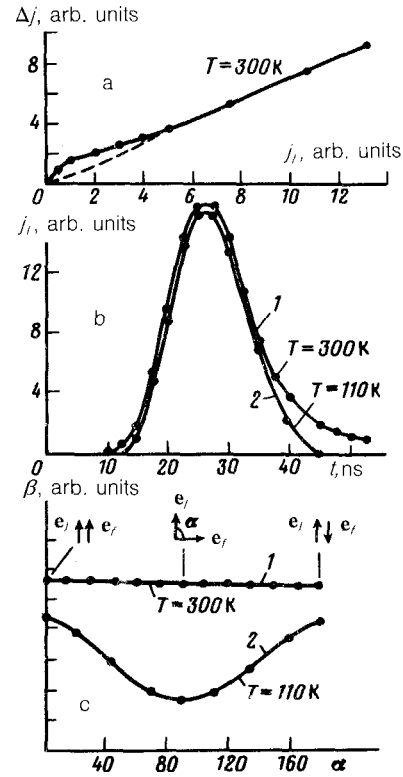

FIG. 3. Light-intensity, time, and polarization dependences of the nonlinear absorption. a: The modulational signal ΔI versus the intensity of the laser light, I_l. b: Shape of the ΔI signal. 1—300 K; 2—110 K. c: β versus the relative orientation of the polarization unit vectors $\mathbf{e}_l$ and $\mathbf{e}_f$. 1—300 K; 2—110 K.

two-photon adsorption in YIG, we carried out a study of the dependence of the spectra on the laser light intentisy i_l and also on the relative orientation of the polarizations of the probe and laser beams (Fig. 3). It was found that the modulational signal ΔI depends in a nonlinear way on the intensity I_l (Fig. 3a). The shape of this signal differs from that of the laser pulse in that its trailing edge is stretched out about 5 ns at the level of $0.1\Delta I^{\max}$ (curve 1 in Fig. 3b). Furthermore, the coefficient β does not depend on the relative orientation of the polarization unit vectors of the laser and flashlamp beams (curve 1 in Fig. 3c). These results indicate that at room temperature the spectrum of two-photon absorption is dominated by two-step transitions through a real electron state in the band gap. At low temperatures, on the other hand, the shape of the modulational signal (curve 2 in Fig. 3b) and the polarization dependences (curve 2 in Fig. 3c) imply that two-photon transitions dominate the shaping of the spectrum.

From the spectra of single-photon absorption of YIG we know[2] that a broad absorption band is observed at energies from ~ 1.15 to ~ 1.60 eV. This band can be unambiguously linked with the electron transition ${}^6A_{1g} \rightarrow {}^4T_{1g}$, between the ground and first excited states of the Fe^{3+} ion in the octahedral sublattice.[2,6] Consequently, a laser pulse with an energy $\hbar\omega_l = 1.17$ eV can cause a real filling of the intermediate ${}^4T_{1g}$ state; this filling will promote an increase in the absolute value of ${}^3\beta$. As the temperature is lowered, however, the single-photon absorption coefficient at the energy 1.17 eV decreases rapidly,[7] and the extent of actual filling of the ${}^4T_{1g}$ state also decreases. As a result, there is a strong temperature dependence (Figs. 1 and 2), and the nature of the two-photon absorption changes from two-step to two-photon.

Despite the pronounced temperature-induced changes in the values of β, the overall nature of the spectrum of β retains the same structure, consisting of three regions (Fig. 1). A corresponding structure of the spectra of two-photon absorption in the direct absorption region has been observed previously in crystals with the perovskite structure[4] (e.g., in $BaTiO_3$ and $SrTiO_3$). In these crystals the structure of the two-photon absorption edge stems from transitions from the valence subbands of the $2p$ band of oxygen to the $3d$ conduction band of titanium. On the basis of the this analogy between the two-photon absorption spectra in YIG and perovskites, and noting that a photoconductivity is observed[8] at ~ 2.9 eV in YIG, we can conclude that the nonlinear absorption spectrum in YIG corresponds to intrinsic direct transitions between the valence $2p$ band of oxygen and the $3d$ conduction band of iron in the octahedral sublattice.

In summary, this study has made it posible, for the first time, to distinguish in YIG a region of $2p$-$3d$ transitions from transitions in Fe^{3+} ions between $3d$ states in the crystal field. This study has also made it possible to accurately determine the band gap: $E_g = 2.66$ eV (at 298 K). It has been found that intermediate electron states of $3d$ ions can play an important role in shaping the two-photon absorption in magnetically ordered crystals. A change in the shape of the moulational signal can be exploited to determine the lifetime of these states. We believe that further studies of YIG and other magnetically ordered dielectrics by the methods of nonlinear spectroscopy will make it possible to solve many important questions regarding their electronic structure.

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