Laser stepped resonant photoelectric effect involving Nd^{3+} dopant ions at the surface of a ZrO_2 crystal

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The possibility of observing a laser stepped resonant photoelectric effect is discussed. Data on a photoemission of electrons from the surface of Nd:ZrO_2 crystals are reported. These data are interpreted as evidence of the observation of this effect.

Laser resonant stepped photoionization of free atoms and molecules has now become quite familiar and continues to attract much research interest.[1] There is considerable interest in efforts to observe a resonant stepped photoionization for dopant particles on a surface.

One can specify a solid-state system for which there exists a set of isolated energy levels between the ground state of the system and its ionization threshold: ions of transition metals with a d or f shell whose filling is nearing completion, in an insulating crystalline matrix. A set of energy levels belonging to the d^n or f^n configuration of the transition-metal ion would arise in such a crystal. A sequential stepped resonant laser excitation of rare-earth ions in matrices has been observed in several places (see, for example, Ref. 2 and the bibliography there). We have undertaken an effort to search for and study the stepped resonant laser photoelectric effect in such media. The idea of the experiment is illustrated by Fig. 1. Laser light can send an ion in the matrix into a high-lying state in various ways. From this state, energy can be transferred to the matrix, in a process accompanied by the formation of an electron above the vacuum level and a subsequent emission of the electron from the insulator (a photoelectric effect).

The test samples were pressed against a metal electrode. Nanosecond laser pulses focused into a spot with an area 7×10^{-3} cm^2 were applied to the sample at an angle of about 45°. A constant voltage between -2.5 and $+2.5$ kV was applied to the electrode with the sample. This voltage directed the photoelectrons (or photoions) to a VÉU-6 photomultiplier with a grounded input. The measurements were carried out in a vacuum chamber pumped by an ordinary diffusion pump through a nitrogen cold trap. The vacuum was on the order of 10^{-5} torr. Some control experiments were carried out in an oil-free vacuum on the same order of magnitude, 10^{-5} torr; no significant differences in the magnitudes of the electron and ion signals were found. All the test samples were cleaved and washed beforehand in alcohol and acetone.

Photoemission from insulating crystals caused by laser light with a power density

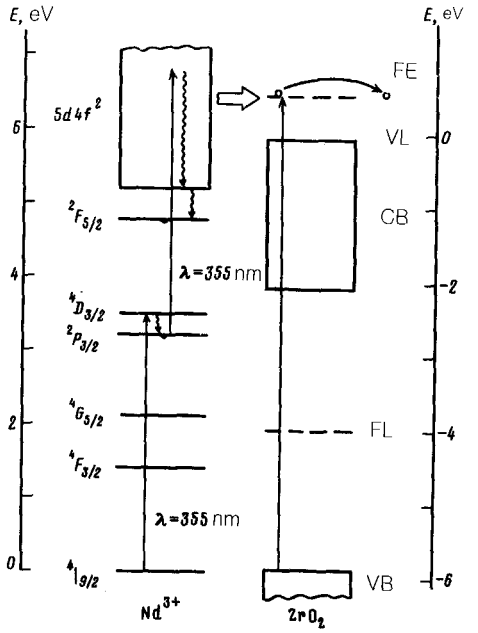

FIG. 1. Laser stepped resonant photoelectric effect. Shown at the left are some of the energy levels of the Nd^{3+} ion in a matrix. The origin for the energy scale is placed at the ground state. Shown at the right is a simplified band structure of the matrix. VB—Valence band; CB—conduction band; FL—Fermi level; FE—free electron; VL—vacuum level. The broad arrow represents the transfer of excitation.

$10^3 < \mathscr{P} < 10^9$ W/cm^2 has been observed previously in several places. This photoemission has been attributed to a nonresonant multiphoton photoelectric effect or to effects associated with small absorbing inhomogeneities.[3,4] For all the test samples and all the wavelengths which we studied, we, too, detected a nonresonant photoemission of electrons and ions. The corresponding experimental material will be reported elsewhere.

Figure 2 shows the photoelectron yield N_{phe} versus the energy of the laser pulses, E_{las}, for the third harmonic of a neodymium-glass laser (the pulse half-width was $T_{1/2} = 15$ ns, and the wavelength was 355 nm). For an activated Nd:ZrO_2 sample (the concentration of neodymium ions was 0.3 at. %; the ZrO_2 crystal was stabilized by the oxide of Gd in a concentration of 16%), we found that the threshold for the appearance of a quadratic dependence of the yield of the photoelectric effect was lower by more than an order of magnitude than the corresponding threshold for the ordinary nonresonant two-photon photoelectric effect (curves 2–4). We observed this situation in all the test samples, including some unactivated crystals. This difference in threshold is not observed when samples are exposed to nanosecond pulses of the second harmonic of a neodymium-glass laser (532 nm) or of a nitrogen laser (337 nm). We attribute this result to the presence of a two-step resonant photoelectric effect in the Nd:ZrO_2 crystal when light with a wavelength of 355 nm is applied to it. Let us look at some corresponding calculations.

The wavelength of 355 nm lies in a transparency region of the ZrO_2 crystal.[5] It causes the following sequence of transitions of the Nd^{3+} ion (Fig. 1): $^4I_{9/2} \rightarrow {}^4D_{3/2}$

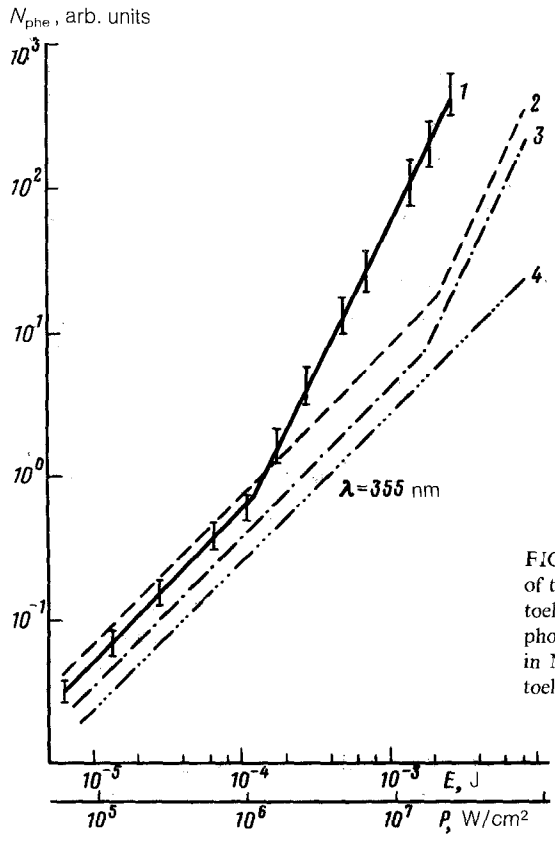

FIG. 2. Yield of photoelectrons versus the energy of the laser pulse. 1—Resonant two-stepped photoelectric effect in Nd:ZrO_2; 2—nonresonant two-photon photoelectric effect in ZrO_2; 3—the same, in Nd:YAG; 4—nonresonant single-photon photoelectric effect in LK-5 glass.

(for which the cross section is on the order of 10^{-19} cm^2); then a rapid, subnanosecond, radiationless relaxation[6,7] $^4D_{3/2} \rightsquigarrow {}^2P_{3/2}$; and a transition from $^2P_{3/2}$ to a level of the $5d\,4f^2$ configuration. The levels of the $5d\,4f^2$ configuration of the Nd^{3+} ion span a very broad energy range (of several thousand reciprocal centimeters) in oxygen crystals, and there are no grounds for believing that the difference between the positions of the *d*-configuration levels in the YAG and ZrO_2 matrices is so large that it would be capable of driving this *f–d* transition away from resonance (see Ref. 8 for data on the levels of the *d* configuration in YAG).

All the spectroscopic parameters of the Nd^{3+} ion pertinent here were measured in Ref. 7 for matrices of YAG, YGaG, and (in part) ED-2 glass. Specifically, the lifetime of the metastable $^2P_{3/2}$ level is $T_{1/2} = 0.3$–0.4 μs; the cross section for the dipole-allowed *f-d* transition is $\sigma \simeq 10^{-17}$–10^{-16} cm^2; and the excited level of the *d* configuration relaxes over 2–5 ns to the long-lived metastable level $^2F2_{5/2}$ ($T_{1/2} \simeq 2$–3 μs), which has an energy $E \simeq 37\,500$ cm^{-1}. One might expect that the values of these parameters for a ZrO_2 matrix would be on the same order of magnitude.

Let us estimate the number of excited Nd^{3+} ions which might contribute to a stepped photoelectric effect. The photoelectron emission depth for most insulators is[9]

1–10 nm. In other words, there are about 10^{11} neodymium ions in the "active zone" of the crystal. Laser light with an energy density E acting on a transition with a cross section σ excites only some fraction η of the illuminated ions. This fraction can be found from the formula $\eta = E\sigma/\hbar\omega$, where $\hbar\omega$ is the energy of the photon. In the case at hand, for a pulse energy of 1 mJ, we find the value $\eta_1 \simeq 2.5 \times 10^{-2}$ for the transition $^4I_{9/2} - {}^4D_{3/2}$ and $\eta_2 \simeq 1$ for the *f-d* transition. In other words, up to 2.5×10^9 ions in the active zone can be excited into levels of the *d* configuration. Under the assumption that most of the photoelectrons observed result from the multistep photoelectric effect, we find that 10^{-5}–10^{-6} of all the ions excited into the *d* configuration generate photoelectrons after a transfer of excitation to the matrix. A "whole" transfer of excitation to the matrix (without an exchange involving many phonons) has been observed previously (in fluorescence of a YVO_4 matrix after two-step excitation of the Nd^{3+} ion at $\lambda = 532$ nm; Ref. 7).

On the basis of data on the work function and band gap of ZrO_2 crystals[10,11] we would expect that a generation of photoelectrons would be possible as a result of the transfer of an excitation with an energy greater than 5–6 eV to the matrix. In our case, the Nd^{3+} ion acquires an energy up to 6.6 eV as a result of two-step absorption. In other words, it acquires an energy which is clearly above the threshold for the photoelectric effect. It may be that an absorption of laser light from levels of the *d* configuration or from the metastable $^2F2_{5/2}$ level of the Nd^{3+} ion is also playing an important role here.

In summary, we have succeeded in finding a test sample ($Nd:ZrO_2$) and conditions for the application of laser light (at $\lambda = 355$ nm in nanosecond pulses) such that the nature of the emission of photoelectrons is quite different from that in other cases which have been studied. We believe that this difference can be interpreted as evidence of a laser resonant stepped photoelectric effect.

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