TWO-PHOTON EXCITATION IN $CaF_2:Eu^{2+}$

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With the development of optical masers,[1-3] it is now possible to study two-photon processes which necessitate intense sources of monochromatic radiation. We have investigated the generation of blue fluorescent light around $\lambda_b = 4250$ A by illuminating $CaF_2:Eu^{2+}$ crystals with red light, $\lambda_r = 6943$ A, of a ruby optical maser.[2] Our experiments differ from the recent investigations by Franken et al.,[4] who observed the generation of optical harmonics in quartz. It is essential in their experiments that the crystal lacks a center of inversion and that it is transparent at ν_r and $2\nu_r$. In our investigations, the highly symmetric cubic CaF_2 structure is used and after an excitation to a real absorbing state of Eu^{2+} at $2\nu_r$, the fluorescent decay to a lower state is observed. CaF_2 crystals, with 0.1% Eu^{2+} ions substituted for Ca^{2+}, exhibit strong absorption between 30 000 and 25 000 cm^{-1} resulting from electronic $4f \rightarrow 5d$ transitions of the Eu^{2+} ion.[5] Excitation of $CaF_2:Eu^{2+}$ with light absorbed in this wavelength range gives rise to a brilliant blue fluorescence (bandwidth ~300 A) which originates at levels around 4200 A and terminates at the ground state. There are no energy levels below 22 000 cm^{-1}, making $CaF_2:Eu^{2+}$ crystals transparent at $\nu = \nu_r$.

We have performed the following experiments. A $CaF_2:Eu^{2+}$ crystal of 1-mm thickness was mounted in front of the entrance slit of a quartz spectrometer, and the light beam of a ruby optical maser (~0.1-joule output) was focused onto the sample. Two red filters with transmission values $T < 10^{-4}$ for $\lambda < 6100$ A were mounted between the maser and the $CaF_2:Eu^{2+}$ crystal in order to eliminate the possibility that blue or ultraviolet stray radiation from the flash lamp reaches the sample. The fluorescence of the crystal was photographed at the exit slit of the spectrometer. Between the sample and the prism, a blue filter with $T \cong 10^{-3}$ at 7000 A was interposed to avoid excessive blackening of the photographic plate. In Fig. 1 a picture of the output spectrum is presented which was obtained by one flash (~500 μsec) of red light. The overexposed bright spot at 6943 A results from the incident maser light. Of particular interest is the observation of light around 4250 A, which is characteristic for the blue fluorescence of $CaF_2:Eu^{2+}$. The width of the blue streak is approximately 0.3 mm corresponding to the diameter of the incident light beam. When pure CaF_2 was illuminated by the optical maser in the same way, no light with $\lambda < \lambda_r$ was observed on the photographic plate. This observation is expected from the high symmetry of the CaF_2 lattice.

In a second experiment, the light beam leaving the quartz spectrometer was intersected by two mirrors in such a way that the red and blue parts of the spectrum were directed separately onto two photomultipliers. The signals of these photomultipliers were displayed simultaneously on a dual-beam oscilloscope. Load resistors of 10^5 ohms in the photomultiplier circuit were employed in order to smooth out the spikes (resulting from the relaxation oscillations) of the ruby optical maser and to allow a direct quantitative comparison between the two signals. In Fig. 2 the signal I_b obtained in the blue part of the spectrum is plotted against the signal in the red I_r, which is a direct measure of intensity incident on the crystal. The empirical line through our experimental points represents the quadratic relation $I_b \propto I_r^2$, which is a strong indication that we are dealing with a two-photon process. From the calibration of our photomultiplier, the number of blue photons at the exit slit of the spectrometer could be estimated to be 5×10^7 photons per flash. This number agrees well with the value of ~10^8 photons per flash estimated from the blackening of the photographic plate shown in Fig. 1.

We believe that in our experiments a real state of the Eu^{2+} ion at $\nu = 2\nu_r$ is excited by a two-photon process. The observed fluorescence is only an indication that the ion was indeed in the excited state. The probability of a process by which an atom is excited by two photons $h\nu_1$ and $h\nu_2$, the sum of which corresponds to an excited state of the atom, was first treated by Goeppert-Mayer in

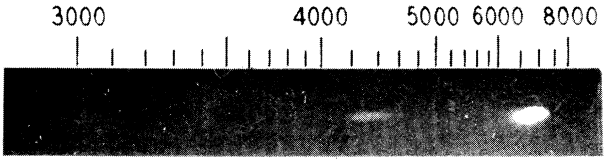

FIG. 1. Positive of photographic plate, indicating the blue emission of a $CaF_2:Eu^{2+}$ crystal under strong illumination with $\lambda_r = 6943$ A.

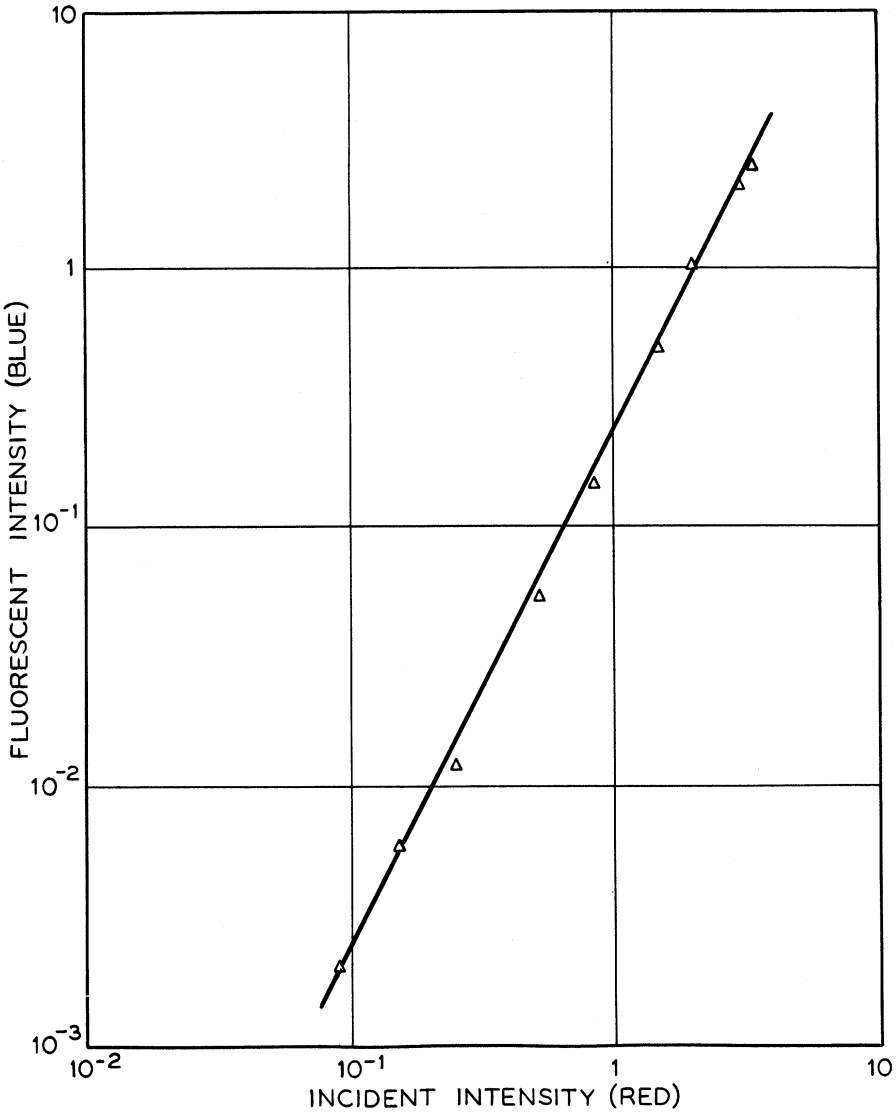

FIG. 2. Blue fluorescent intensity of sample versus incident red intensity.

1931.[6] More recently Kleinman[7] has reinvestigated the problem and has derived an equation for the cross section σ for such a two-photon excitation process which allows a direct quantitative estimate of the expected number of blue photons:

$$\sigma = (e^2/mc^2)^2(\lambda_r^2/n^2\Delta\nu)F, \quad (1)$$

where $e^2/mc^2 = 2.8\times10^{-13}$ cm, n is the dielectric constant of the material, $\Delta\nu$ is the width of the absorption band around $2\nu_r$, and F is the incident photon flux. The number of excitations or, assuming a fluorescent quantum efficiency of one, the number of emitted fluorescent photons per unit volume of the specimen is

$$P_b = \sigma NF = (e^2/mc^2)^2(\lambda_r^2/n^2\Delta\nu)NF^2. \quad (2)$$

Here N denotes the number of fluorescent ions in the crystal. For an estimate of P_b, the following experimental data were used: $\lambda_r = 7\times10^{-5}$ cm, $n(CaF_2) = 1.4$, $\Delta\nu = 1.5\times10^{14}$ sec^{-1} (5×10^3 cm^{-1}), and $N = 2.4\times10^{18}$ Eu ions per cm^3. The maser output of 4×10^{17} photons was concentrated into an area of approximately 10^{-3} cm^2; the incident photon flux F is, therefore, $F = 8\times10^{23}$ photon cm^{-2} sec^{-1}. From Eq. (2) we obtain $P_b = 10^{18}$ photons cm^{-3} sec^{-1}. Since the active volume was 10^{-4} cm^3, one calculates 5×10^{10} blue photons to be emitted per flash (500 μsec). The efficiency of this two-photon process is therefore ~10^{-7}. This value could be greatly increased if a system with a narrower excited state (smaller $\Delta\nu$) were employed. For a comparison with the observed number of blue photons, one has to consider the $f/4$ lens system and a number of reflection losses in the spectrometer. The number of photons leaving

the instrument is calculated to be 10^8. This value agrees quite well with the experimentally observed photon flux, giving strong support to the interpretation of our observations. The agreement is better than expected considering the simplifications made in the derivation of Eq. (2) and the estimates made during its application.

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MAGNETIC BREAKDOWN IN CRYSTALS*

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To establish the various regimes of behavior of electrons in a magnetic field, the cyclotron frequency ω_c is usually compared with τ^{-1}, $\hbar^{-1}kT$, or $\hbar^{-1}E_F$, where τ is a typical relaxation time and E_F the Fermi energy. Comparison of ω_c with $\hbar^{-1}E_g$, where E_g is an energy gap of the pertinent band structure, has not been discussed except to note that the usual derivations of an effective Hamiltonian[1] for the motion of electrons in a magnetic field is no longer valid when $\hbar\omega_c \sim E_g$. No attention has been directed to the question of what actually happens when $\hbar\omega_c$ exceeds E_g; that is the subject of the present Letter.

The splitting of the energy levels due to magnetic fields is of the order of 10^{-8} ev per gauss, whereas gaps in ordinary band structures are rarely as small as 0.1 ev. Our question would be academic were it not for the existence of small gaps of the order 10^{-3} ev or less in some metals because of spin-orbit splitting[2] or of points of accidental degeneracy at or near the Fermi level.[3] These gaps are small compared with the Fermi energy and the remaining typical gaps in the band structure. In such a case the answer to our question is that as H increases, one passes from electron orbits determined semiclassically from the entire band structure to those determined semiclassically by ignoring the small gaps. We call this effect magnetic breakdown. Of course, some additional effects take place, i.e., a spreading of the magnetic levels into narrow bands and additional scattering processes, but these are not significant except in the transition range of magnetic field $\hbar\omega_c \sim E_g$.

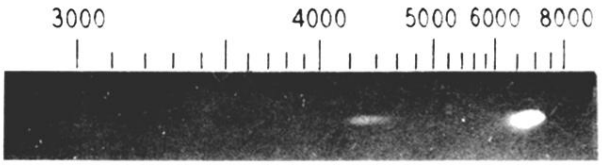
Let us consider a simple example of a free-electron metal perturbed by a one-dimensional periodic potential. The one-electron Hamiltonian in the presence of a magnetic field in the z direction is

$$\mathcal{H} = \frac{1}{2m}\left(\vec{p} + \frac{|e|}{c}\vec{A}\right)^2 + V_0 \cos\kappa x,$$

where

$$\vec{A} = (0, Hx, 0), \quad k_F \gtrsim \kappa.$$

Since the electron distribution overlaps into the second zone, the Fermi surface consists of an undulating cylinder in the first zone with axis in the x direction and a small pocket of electrons in the second zone [Fig. 1(b)]. When H is small, i.e., $\hbar\omega_c \ll V_0$, the undulating cylinder gives rise to a set of open orbits; as consequences de Haas–van Alphen oscillations arise from the pocket but not from the cylinder and the R_{xx} component of the resistivity tensor increases quadratically with H. When $\hbar\omega_c \gg V_0$,[4] magnetic breakdown essentially restores the free-electron surface [Fig. 1(a)] and only the equatorial section of the "sphere" gives rise to a de Haas–van Alphen period. Moreover, because the open orbits have now disappeared, R_{xx} decreases as H^{-2} to a saturation value which is very approximately the free-electron value. The spreading of the magnetic levels into bands, which have a maximum width of about $2V_0$ for orbits which just intersect the zone faces, gives no appreciable effect, and the additional scattering processes give only second order corrections to the free-electron magnetoresistance[5]



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