

FIG. 3. Ratio of the integrated intensities of the  ${}^5D_0 \rightarrow {}^7F_0$  to the  ${}^5D_1 \rightarrow {}^7F_0$  fluorescence versus temperature.

ed elsewhere,<sup>6</sup> presents the characteristic behavior expected from thermalized levels.<sup>1</sup>

To substantiate further our observations we measured the ratio of the integrated intensities of the  ${}^5D_1 \rightarrow {}^7F_0$  to the  ${}^5D_0 \rightarrow {}^7F_0$  fluorescence, from 15 to 600°K, with the system under continuous optical excitation. The results are reported in Fig. 3. The increase in the ratio up to ~80°K is due to the increase of the  $D_2 \rightarrow D_1$

decay rate in that region. Above 80°K the ratio decreases because of the depopulation of  ${}^5D_1$  through  $D_1 \rightarrow D_0$  decay (we notice here that the  ${}^5D_0$  lifetime is almost constant and equal to ~1.6 msec up to 300°K). At about 330°K a turning point occurs and the ratio starts increasing with temperature, because of the fact that upward phonon annihilation processes become more and more relevant. Finally from ~400°K up the ratio follows a Boltzmann law, indicating the presence of the thermalization condition. This, on the other hand, is the temperature at which the  ${}^5D_0$  and  ${}^5D_1$  decays start presenting equal time constants.

Both the pulsed-fluorescence and the continuous-fluorescence data provide direct evidence of phonon annihilation processes in the excited states of  $\text{BaClF:Sm}^{2+}$ .

†Work sponsored by U. S. Army Signal Research and Development Laboratories, Fort Monmouth, New Jersey, under Contract No. DA-44-009-AMC-1090(T).

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## TWO-PHOTON ABSORPTION SPECTRUM OF CuCl

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(Received 21 September 1967)

Two-photon measurements were done on single crystals of CuCl at 20°K in an energy range from 3.2 to 4.3 eV. For the first time sharp exciton lines are found in a two-photon spectrum. A detailed study of the polarization dependence yields symmetry assignments of the exciton states.

Two-photon spectra have first been measured by Hopfield and Worlock<sup>1</sup> on KI and CsI; subsequently other ionic crystals ( $\text{TlCl}$ ,<sup>2</sup>  $\text{RbBr}$ ,  $\text{RbI}$ ,  $\text{KBr}$ , and  $\text{NaBr}$ <sup>3</sup>), a semiconductor ( $\text{CdS}$ <sup>4</sup>), and a molecular crystal (anthracene<sup>5</sup>) were investigated. The spectra of CdS and the ionic

crystals show a very similar behavior: The two-photon spectra start in the region of the band gap and rise towards higher energies without indicating any pronounced structure. No resolved exciton lines have been seen in these spectra. There is some structure found in the

spectrum of anthracene, which could be attributed to molecular vibrations.

In this Letter we present a very different two-photon spectrum. It is measured in CuCl, which has zinc-blende structure ( $T_d$ ) and thus no inversion symmetry. Therefore the exciton states are of mixed parity. The exciton lines observed in one-photon absorption<sup>6</sup> can in this case also be expected in the two-photon spectrum. We have measured the two-photon spectrum of single crystals of CuCl at 20°K in a spectral region from 3.2 to 4.3 eV using a Q-switched Nd laser and a xenon flash lamp as a tunable source.<sup>7</sup> The crystals were grown from the vapor in evacuated tubes at 380°C.<sup>8</sup> As shown in Fig. 1, the spectrum reveals the typical behavior near the gap, in this case from about 3.4 eV to higher energies. Below the band gap, however, we find two sharp exciton lines. The energies of these lines are 3.210 and 3.292 eV, which coincide quite well with the corresponding exciton lines in the one-photon spectrum. These two-photon experiments allow the exciton bands to be determined by direct absorption measurements in large single crystals—the length of our crystals was 10 to 15 mm. Previously the exciton lines could only be obtained from transmission measurements on evaporated thin films or from reflectivity data. Though we were able to measure the spectrum with a resolution of 5 Å, it still seems to be necessary to improve this resolution in order to get the true width of the first

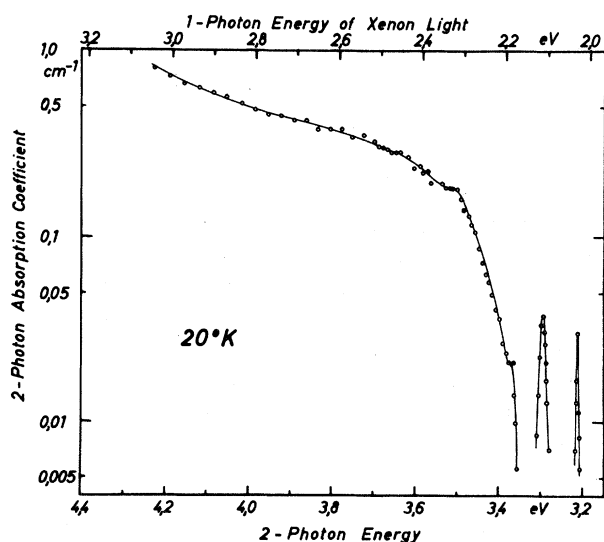


FIG. 1. Two-photon absorption spectrum of CuCl. Laser flux:  $10^{26}$  photons/cm<sup>2</sup> sec.

exciton line.

In addition we have done a detailed study of the polarization dependence of the two-photon absorption. These data, as measured in the second exciton peak, are shown in Fig. 2. The absorption coefficient is plotted as a function of the xenon light polarization for two fixed laser polarizations. The same polarization behavior is found in the first exciton peak. We analyzed these measurements using the formalism of Inoue and Toyozawa.<sup>9</sup> In a crystal with  $T_d$  symmetry, final levels of  $\Gamma_1$ ,  $\Gamma_3$ ,  $\Gamma_4$ , and  $\Gamma_5$  symmetry at  $k=0$  are allowed in two-photon absorption from a  $\Gamma_1$  ground state. Figure 2(a) shows a  $\sin^2\alpha$  dependence (solid line) to be in good agreement with the experiments, excluding  $\Gamma_1$  and  $\Gamma_3$  from the four two-photon allowed symmetries. A decision between the remaining symmetries  $\Gamma_4$  and  $\Gamma_5$  can be gained from a measurement with a laser polarization of 135° [Fig. 2(b)]. The experimental points agree well with a  $\frac{1}{2}(1-\sin 2\alpha)$  angular dependence (solid line), leaving  $\Gamma_5$  as the only possibility which is consistent with the experiments.

Using the adopted assignments of the upper valence bands<sup>10</sup> at the  $\Gamma$  point in the Brillouin zone ( $\Gamma_7$  and  $\Gamma_8$ ) and of the lowest conduction band ( $\Gamma_6$ ), we can determine the symmetry of

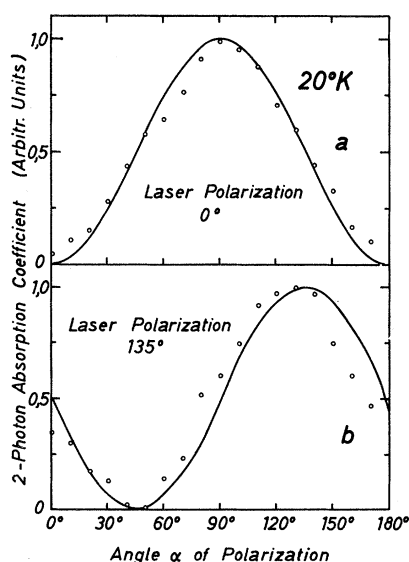


FIG. 2. Two-photon absorption of CuCl at 3.29 eV as a function of the xenon light polarization for indicated fixed laser polarization. The 0° direction of polarization is referred to the [100] crystal direction; the light beams are incident along [001].

the exciton states by taking the product of the hole ( $\Gamma_7$  or  $\Gamma_8$ ) and the electron ( $\Gamma_6$ ) symmetries under the assumption of an *s* envelope. From  $\Gamma_7 \times \Gamma_6 = \Gamma_2 \oplus \Gamma_5$  we get  $\Gamma_5$  for the first exciton as the only two-photon allowed symmetry, which is consistent with our analysis of the polarization dependence. For the second exciton we get  $\Gamma_8 \times \Gamma_6 = \Gamma_3 \oplus \Gamma_4 \oplus \Gamma_5$ , which are all two-photon allowed. Our experiments show that the  $\Gamma_5$  transition is the dominant one. Measurements of the polarization dependence in the band (3.5 eV) gave very different results, indicating a rather complex symmetry behavior of the involved band states.

We would like to thank Professor W. Martienssen and Professor H. J. Queisser for stimulating discussions. Thanks are also due to J. U. Fischbach for help during the experiments. The financial support of this project and the "Frankfurt Unit for Crystal Growing" by the Deutsche Forschungsgemeinschaft is greatly

appreciated.

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## CONDUCTION-ELECTRON CONTRIBUTIONS TO THE HYPERFINE FIELDS IN METALLIC Eu AND Gd

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(Received 21 August 1967)

The Mössbauer effect of the 21.7-keV  $\gamma$  line of  $\text{Eu}^{151}$  has been employed to study the isomer shifts and the magnetic fields in Eu-Yb alloys. From these measurements the conduction-electron contribution to the hyperfine field at the Eu atom in Eu metal due to its own 4*f* electrons and due to its neighboring atoms can be deduced. In addition an explanation is given for the apparent lack of conduction-electron contribution to the observed hyperfine field in metallic Gd.

Mössbauer effect studies are very well suited for the investigation of metal and alloy systems, since they measure simultaneously the spin and the charge density at the nucleus.<sup>1</sup> Considerable information has been obtained by these types of experiments about transition-metal and alloy exchange interactions.<sup>2-4</sup> In the rare-earth (R.E.) region, so far the most important information<sup>5</sup> has been obtained from Knight-shift measurements on diamagnetic ions alloyed with R.E. ions. From these experiments a negative exchange interaction between 4*f* and conduction electrons (C.E.) was deduced and interpreted as being due to interband mixing.<sup>6</sup> On the other hand, the calculations of Watson and Freeman<sup>7</sup> and the observed hyperfine fields

in Eu and Gd intermetallic compounds<sup>8</sup> which are notoriously less negative than the corresponding fields in a diamagnetic ionic environment suggest a positive C.E. polarization at the site of the magnetic ion. In this paper, to our knowledge, for the first time the C.E. polarization contribution to the hyperfine field in a magnetically ordered metal (Eu metal) can be separated into the effects produced by the electrons of the ion itself and the effects due to neighboring ions. It will be seen that while the effect due to the neighbors (as seen, for example, by diamagnetic Al ions) is indeed negative,<sup>5</sup> there is a large positive contribution at the site of the magnetic ion due to the C.E. polarization by its own 4*f* electrons. On the