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Microwave Absorption of Semiconducting Cadmium Fluoride at 77°K

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The microwave absorption of semiconducting $CdF_2:Gd^{3+}$ crystals at 77 °K was measured from 0.1 to 11 GHz, and at 17.5 and 37 GHz. σ_{mi} increases with frequency at an increasing rate in the 0.1–10-GHz region. At higher frequencies, σ_{mi} decreases with increasing frequency, indicating the presence of a conductivity peak near 12 GHz which may arise from intertrap tunneling of semiconducting electrons. Absorption from 40 GHz to 3×10^{12} Hz may originate from the hopping process.

Kingsley and Prenner[1] discovered in 1962 that CdF_2 with a trivalent dopant can be made semiconducting by baking in cadmium vapor. Since then many electrical, magnetic, and optical studies have been made on this semiconductor.[2–9] Eisenberger *et al.*[2] observed near-[5] and far-infrared[3] photoconductivity and a large polaron mass[2] in the microwave region. In this paper, the microwave absorption spectrum of semiconducting CdF_2 from 0.1 to 37 GHz is reported. These experimental data intend to bridge the gap from the dc electrical to the far-infrared data and are interpreted to explain the semiconducting mechanism, especially in the far-infrared and cyclotron-resonance regions.

The main features of the data are (i) the presence of a microwave absorption peak near 12 GHz, (ii) higher low-frequency background absorption, e.g., the absorption at 3 GHz is greater than absorption at 37 GHz, and (iii) indication of a smooth extrapolation of ac conductivity from the far infrared down to about 40 GHz. These features may be interpreted, respectively, as (a) tunneling of semiconducting electrons from one trap to the other (e.g., intertrap tunneling), (b) band conduction of polarons, and (c) electron hopping on cations around the trivalent dopant.

Two measuring techniques were employed: the transmission technique below 10 GHz and the resonance-cavity method for frequencies at 10.8, 17.5, and 37 GHz. In the transmission-line method, semiconducting $CdF_2:Gd^{3+}$ single crystals 2 mm in diameter and 0.2–1.5 mm in thickness were electroded on opposite flat faces by rubbing with In-Hg amalgam or hot indium solder. Samples were mounted directly on an OSM connector at one end of a 50-Ω coaxial line. The line had Teflon insulation with solid copper shield and was submerged in liquid nitrogen at the sample end. Hewlett-Packard model No. HP 8410A network analyzer, model No. HP 8411A harmonic frequency converter, and model No. HP 8741A or HP 8742A reflection test units were used to display the series impedance between 0.1 and 10 GHz on the Smith chart. The series impedance of the sample at each frequency was deduced by comparing two measurements, one with the sample at the end of the transmission line and the other with the end short-circuited. From the measured series impedance of the sample, the equivalent parallel resistance of the sample and hence the corresponding microwave conductivity $\sigma_{mi}(f)$ was calculated. The data up to 6 GHz, where $\sigma_{mi}(f)$ rises appreciably, have been checked by comparing the semiconducting sample with an identical, except unconverted, CdF_2 at the end of another "identical" transmission line. This method, however, cannot be used above 6 GHz

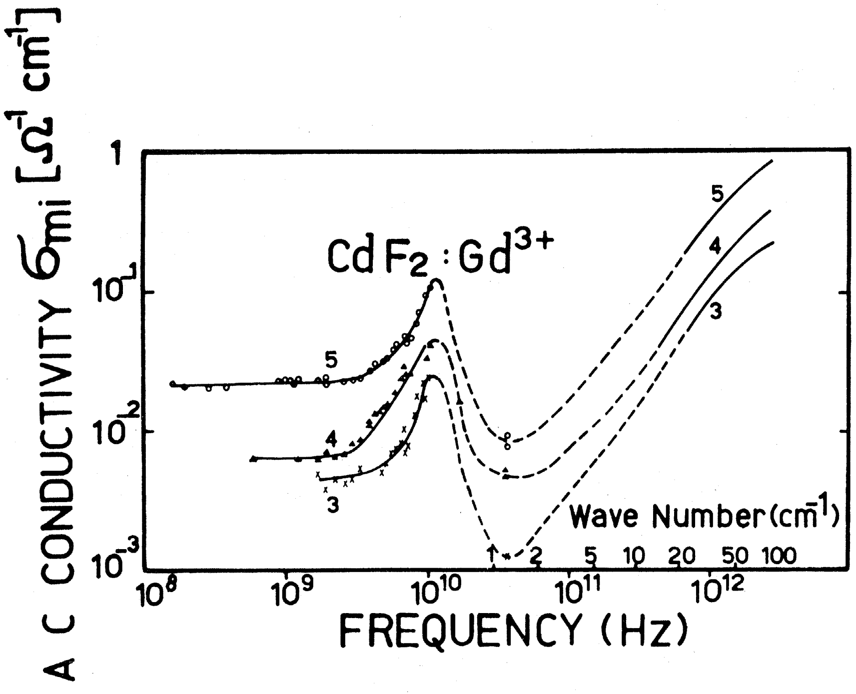

FIG. 1. ac conductivity vs frequency of semiconducting $CdF_2 : Gd^{3+}$. The microwave data are at 77 °K and the far-infrared data of Bosomworth *et al.* (Ref. 2) are at 1.7 °K for samples 5 and 3 and at 77 °K for sample 4. Samples 3–5 differ in room-temperature electron concentration from 10^{17} cm^{-3} to 8×10^{17} cm^{-3}.

because of the increasing difference in electrical length introduced by the minor difference in the physical length and connectors between the two lines. For checking the transmission-line data near 10 GHz, we used the resonance-cavity method at 11 GHz with samples of 0.15 mm thick×1 mm^2 or less in a TE_{011} cylindrical cavity 3.3×3.8 cm in diameter. The data from both the transmission-line and cavity techniques around 10 GHz agree well within the experimental error.

Figure 1 shows the frequency spectrum of microwave conductivity of semiconducting CdF_2:Gd^{3+} crystals at 77 °K. Samples of three different carrier concentrations were used. They are labeled, according to decreasing concentration, as samples 5, 4, and 3 in Fig. 1 and are equivalent to the samples for curves 5, 4, and 3, respectively, in the far-infrared absorption spectrum.[2] Sample 5 appeared bluish and was converted from Cole's sample. Samples 4 and 3 were used by Bosomworth *et al.*[2] for curves 4 and 3, respectively, in the far-infrared spectra.[2] The frequency in Fig. 1 covers from 0.1 to 11 GHz continuously with points at 17.5 and 37 GHz.

In view of the scattering of the data and the difficulties involved in obtaining more frequency points in the 10–40-GHz cavity region, the accuracy of the data is discussed briefly. In the region of transmission technique, i.e., below 11 GHz, the range of error increases with the measuring frequency and with the decreasing concentration of the semiconducting electrons in the sample. This error mainly comes from the contact resistance of the electrodes on the sample. For example, the error at 10 GHz of samples 5, 4, and 3 are about 10, 20, and 40%, respectively. The range of error in the cavity measurement can be as large as 50%, which is introduced by the inaccuracy in the location and the size of the sample. The size of the sample for obtaining a convenient resonance curve on the oscilloscope is determined by the conductivity of the sample. Namely, a conductive sample must be smaller in size and vice versa.

As mentioned previously, the microwave data in Fig. 1 indicate the presence of an absorption peak near 12 GHz. This is perhaps the first direct observation of a microwave absorption peak in solids where no external magnetic field is applied. The origin of this peak is not known. It is tentatively suggested that the peak is due to tunneling of semiconducting electrons between traps. From previous studies,[1–5] the conduction electrons in the semiconducting CdF_2 are known to be trapped at low temperatures by the attractive Coulomb potential of the trivalent dopant. These electrons do not actually sit on the dopant. Instead, they are on the neighboring Cd^{++} ions because of their large electron affinity. The absorption peaks due to transitions within the potential well of the trap (intratrap transitions) are in the far- and near-infrared regions.[2] A microwave absorption peak may be expected from intertrap transitions[2] or intertrap tunneling, where the trapped semiconducting electron tunnels from the potential well of one trap to that of the other trap. The distance involved in the intertrap transition is generally larger than in the intratrap transitions. The intertrap transition can, therefore, occur in the microwave, instead of the infrared region. Eisenberger *et al.*[2] have used intertrap transitions to explain the far-infrared background absorption of semiconducting CdF_2. Instead, one is inclined to apply their intertrap treatment to interpret the microwave absorption peak at 12 GHz in Fig. 1. Later, the far-infrared broad background[2] which lies in the right-hand portion of Fig. 1 and rises with increasing frequency is explained to be due to electron hopping around the Gd impurity.

A close inspection of the background absorption in Fig. 1 reveals that the background is essentially flat at frequencies below 3 GHz, and then gradually drops with increasing frequency as indicated by the point at 37 GHz. The intertrap transition is probably not responsible for this background behavior. It is speculated that this background absorption is due to free polarons[10] moving in a narrow band. This interpretation is supported by the following observations: First, the frequency dependence of the background absorption, i.e., flat at low frequencies with high-frequency cutoff, resembles that of free carriers[10,11] moving in the conduction band. Second, the cutoff frequency of the background absorption is reasonably close to the relaxation time $\tau = 10^{-11}$ sec or $f \approx 16$ GHz of the moving polaron as deduced from cyclotron-resonance experiments.[2] The remaining portion of Fig. 1, from microwave data at 37 GHz to Bosomworth's far-infrared data[2] up to 3×10^{12} Hz, unfortunately has a large frequency gap from 40 to 500 GHz, wherein no experimental data are presently available. The microwave data at 37 GHz, however, seem to be naturally located at a low-frequency extrapolation of far-infrared absorption curves. One therefore assumes that the data in this entire region are due to one single conduction mechanism, i.e., electron hopping[12–14] on neighboring Cd ions around the trivalent dopant.

In conclusion, the frequency spectrum of the ac conductivity of semiconducting CdF_2 at 77 °K has the following features: (i) the microwave absorption peak near 12 GHz, (ii) polaron band conduction with a relaxation time ~ 10^{-11} sec, and (iii) electron hopping between cations around the trivalent dopant with a relaxation time ~ 10^{-13} sec, which is shorter than that for band conduction, 10^{-11} sec, as normally expected.[12]

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