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TEMPERATURE DEPENDENCE OF PHOTOCONDUCTIVITY IN CdCr₂Se₄ (*)

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Résumé. — On a mesuré les variations de la photoconductivité (PC) avec la température (T) entre 80° et 330 °K, dans le cas de CdCr₂Se₄ dopé de In, avec, ou sans lacunes de Se. Sans In ou bien dans le cas d'absence de lacunes de Se, la PC est un phénomène activé. En présence de tous les deux la PC varie d'une façon plus compliquée. Les variations de la PC sont attribuées aux changements de la durée de vie plutôt qu'aux changements de la mobilité. L'anomalie dans la courbe de PC en fonction de T^{-1} observée au voisinage de T_c indique que la durée de vie dépend de l'ordre magnétique.

Abstract. — The temperature (T) dependence of the photoconductivity (PC) in CdCr₂Se₄ has been measured as a function of In doping with and without Se deficiencies from 80 to 330 °K. In the absence of Se deficiencies or In, the PC is an activated process over much of the T range. When both are present, the PC behavior is more complicated. The PC variations are attributed to lifetime effects rather than to mobility changes. A break in the PC versus T^{-1} curve, observed near T_c , reflects a dependence of lifetime processes on magnetic ordering.

The electrical transport and optical properties of the ferromagnetic semiconducting spinel CdCr₂Se₄ have attracted much interest [1-9]. The measurement of the temperature dependence and spectral response of the photoconductivity (PC) were undertaken to help resolve questions concerning the nature of the energy levels and the temperature dependence of the mobility. A comparison of PC data to that of electrical transport [1-4] and optical absorption [8, 9] would be especially fruitful.

In this paper the temperature dependence of the photoconductivity of single crystals of undoped [10] and In-doped CdCr₂Se₄ is presented. A temperature dependence for PC occurs for a variety of reasons. If surface recombination and the optical parameters are assumed to be relatively temperature independent, then PC variations with T can be attributed to the temperature dependence of the free-carrier lifetime τ , of the free-carrier mobility μ , or of the position and nature of an excited state (e. g., the thermal dissociation of an exciton). A theory of Haas [5] predicts that spin-disorder scattering produces a minimum in μ at T_c and that as T is lowered below T_c this μ rises dramatically (e. g., by a factor of almost 150 between 120° and 100 °K). PC data on n-type Eu chalcogenides by Bachmann and Wachter was presented as evidence for such a μ behavior [11]. However, most transport data [2, 4] for CdCr₂Se₄ have failed to support this prediction about μ .

The temperature dependence of the PC is shown in figure 1 for pure and In-doped as-grown CdCr₂Se₄. Stoichiometric samples with and without In doping are p-type conductors. The PC of undoped CdCr₂Se₄ increases sharply with decreasing T down to 250 °K where it maximizes. Since no significant spectral [8, 9] or μ changes [2, 4] have been observed in this T range, the PC behavior is ascribed to lifetime effects. Below about 200 °K the PC appears activated with activation energy of 0.16 eV above $T_c = 130$ °K and 0.09 eV below T_c . The lack of a drastic PC increase near

T_c shows that no great change occurs in μ . The change in slope near T_c may be related to a change in lifetime mechanism and/or reflect an energy level shift associated with magnetic order. Such an energy shift is observed in absorption edge [8, 9] and present PC

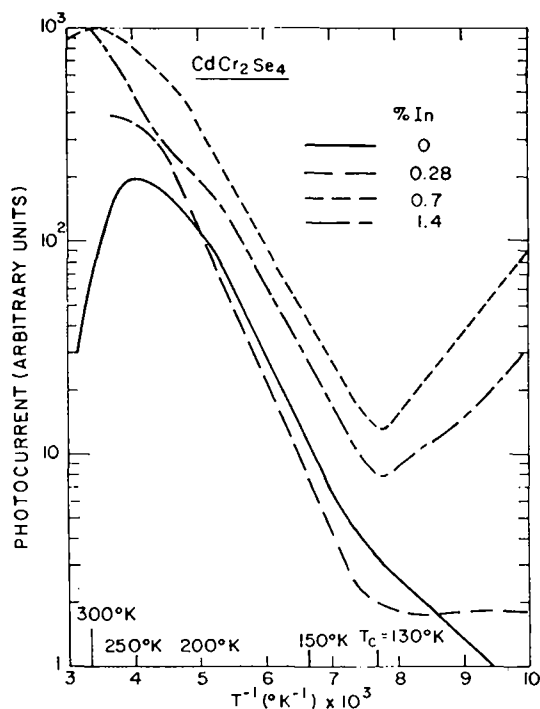


FIG. 1. — Photoconductivity vs reciprocal temperature for stoichiometric CdCr₂Se₄ doped with In.

measurements. Examples of PC spectra taken at 128 and 300 °K are shown in figure 2. The temperature dependence of the lowest energy edge shows a red shift similar to that observed for the absorption edge [8, 9]. These data will be discussed in a future paper.

As In is added (up to 2.7 %) the PC maximum shifts monotonically from 250 °K to higher T . The activation energy below 200 °K is also dependent upon

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In content and has values of between 0.10 and 0.22 eV. We find that this energy initially rises and then falls with increasing In content. Near T_c the slope changes. The dependence of the low T slope $d \ln PC/d(1/T)$ on In content is dramatic and rises from -0.09 eV for no In to $+0.1$ eV for 2.7 % In. With the exception of the 1.4 % In sample, which was felt to be slightly Se deficient, the change is monotonic.

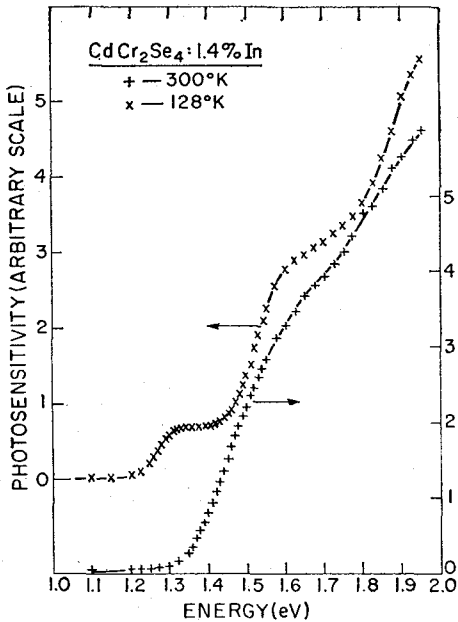


FIG. 2. — Photoconductive spectral response for CdCr_2Se_4 .

Transport data have failed to indicate any drastic μ behavior below T_c [2, 4]. The lack of striking changes in the PC data for undoped CdCr_2Se_4 corroborates this conclusion and suggests that the T dependence is due to lifetime effects. In fact, the behavior of PC with In content is reminiscent of that seen for p-type InSb with increasing donor concentration [12]. The InSb data are understood in terms of lifetime effects. The In doped into CdCr_2Se_4 is then the electron donor. The changes in slope (see Fig. 1) always occur near T_c , whereas in InSb they vary with impurity content [12]. The fact that this change always occurs near T_c may reflect a dependence of an impurity's energy level upon magnetic ordering. The maximum in PC for p-type InSb resulted from a competition between an Auger process dominant in the high- T , intrinsic region and a trapping process in the intermediate- T , extrinsic region. The much larger bandgap for CdCr_2Se_4 precludes direct comparison with InSb. If an Auger process is important for CdCr_2Se_4 , it must be due to ionization of extrinsic levels in these highly impure (by semiconductor standards) materials.

The introduction of a Se deficiency by heat treating the samples in vacuum or H_2 atmosphere [13] produces notable changes in PC as shown in figure 3. The p-type undoped sample, which had a usual semi-conductive resistivity, has a PC curve similar to the stoichiometric In-doped samples. The PC maximum shifts up to room T and the low T slope increases to -0.03 eV while the intermediate T slope is

-0.13 eV. We conclude that the Se deficiency also acts as an electron donor. Without an independent estimate of the Se deficiency, comparisons between these and the In donors are difficult. The production of Se-deficiencies in the In-doped samples changes the

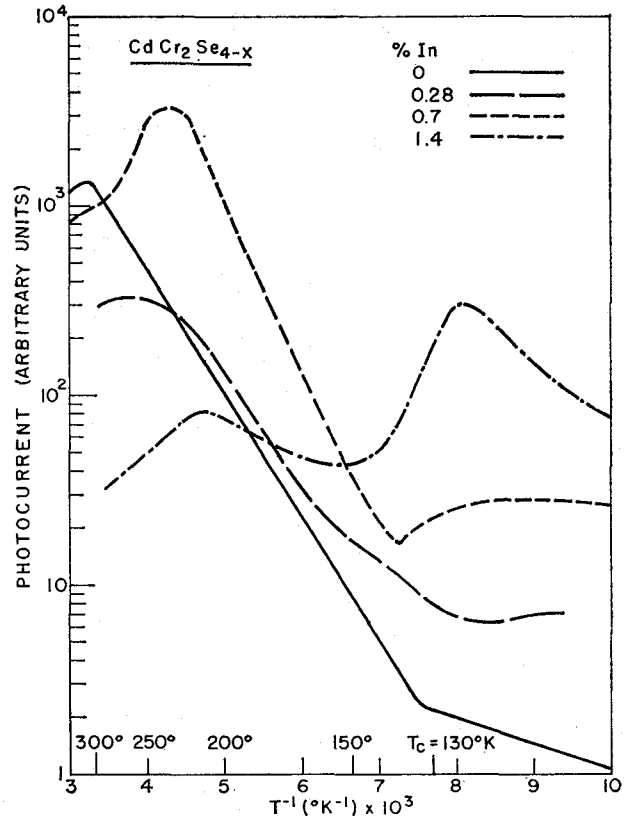


FIG. 3. — Photoconductivity vs reciprocal temperature for Se-deficient CdCr_2Se_4 doped with In.

conductivity to n -type and causes very unusual transport property temperature dependencies [2-4]. The PC is likewise affected. The monotonic increase of the PC maximum to higher T with In content is reversed and a decrease from 300 to 200 °K is observed. This trend is similar to that seen in this T range for a minimum in the Seebeck Q [4]. At lower T , for samples which show a reasonably linear portion, the activation energy is 0.13 ± 0.03 eV. A non-linearity develops into a minimum with increasing In content between 135 and 155 °K. No correlation between the T of this minimum and In content is noted; this may reflect the lack of control in the degree of Se deficiency. This T range is very significant since a maximum in resistivity coincident with a maximum in the Seebeck Q occurs here [2, 4]. At lower T the PC increases non-linearly with decreasing T and either saturates or maximizes, depending on In content. Sample-to-sample variations are great. The curve shown for 1.4 % In doping is an extreme behavior and is included for that reason. Other samples with 1.4 % In content had curves which behaved more like that for 0.7 % In, with many intermediate behaviors also observed. The low T maximum occurs near 120 °K where a sharp minimum in Seebeck Q was observed [4]. It is evident from these curves that no great μ change is observed.

Photovoltaic effect measurements on the 0.7 % In doped sample of this series show a T dependence quite similar to that of the PC.

We conclude that the T dependence of the PC reflects primarily changes in τ rather than changes in μ . Although a relationship between τ and magnetic

order seems established, a specific model for this is not yet available.

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