n-type $CdCr_2Se_4$: A Mott extrinsic semiconductor

M. Héritier
Laboratoire de Physique des Solides, Université de Paris-Sud, Centre d'Orsay, 91405 Orsay, France*
(Received 21 May 1982)

Recent photoemission studies in $CdCr_2Se_4$ give direct evidence for the transport of excess electrons in a narrow d band. This implies that the large anomalies in optical and transport properties near the Curie point are not due to s-d exchange, but to strong d-electron correlations.

Eight years ago it was proposed that n-type $CdCr_2Se_4$ was a Mott extrinsic semiconductor,[1–5] i.e., that excess electrons, due to nonstoichiometry or impurity doping, propagate in a strongly correlated narrow d band. In this model, strong electron-electron correlations can explain the large anomalies observed around the Curie point of this ferromagnetic semiconductor: "Red shift" of the optical-absorption-edge,[6] increase of the mobility and of the number of carriers[7] with increasing magnetic order, etc.

On the contrary, in all the other existing theories,[8–11] these effects are ascribed to s-d exchange, probably because they are somewhat reminiscent of those observed in rare-earth chalcogenides, where this kind of theory is adequate. In these more or less sophisticated versions of the s-d model, it is assumed that conduction takes place in a broad band coupled by exchange to $3d$ or $4f$ localized magnetic moments.

Although both kinds of theory lead to roughly similar behaviors of the conductivity versus temperature, the d-d correlation model predicts a *qualitatively* different behavior if one looks at more detailed features, for which experimental data are now available. In particular, (i) the mobility increases monotonously with increasing magnetic order,[3,12] as observed in $HgCr_2Se_4$ (Refs. 13 and 14); (ii) the optical-absorption edge exhibits a complex critical behavior, without term proportional to the magnetization,[15] as observed in $CdCr_2Se_4$ (Ref. 16); and (iii) the excess electron density of states does not undergo a simple translation but a strong modification of its shape when the ferromagnetic order sets in[3,17] as shown by precise optical measurements in $HgCr_2Se_4$.[18]

In spite of these indirect evidences in favor of the d-d correlation model, currently published interpretations of $CdCr_2Se_4$ properties rely on the s-d exchange. The recent photoemission studies of Miniscalco *et al.*[19] determine the position of the d bands in $CdCr_2Se_4$: The filled t_{2g} band lies below the top of the broad valence band. The e_g band is the lowest empty band, in accord with the band model of Refs. 1–5. The density of states of Miniscalco *et al.*[19] is identical with that of Ref. 3, Fig. VI-9, drawn eight years ago. This energy-band scheme rules out the interpretations based on s-d exchange. If s-d or p-d exchange played any role in $CdCr_2Se_4$, anomalies would be expected in the case of conduction in the broad valence band, i.e., in p-type samples, at variance with the data. Of course the effects observed in the case of n-type conduction in the d band cannot be ascribed to s-d exchange. The experiments of Miniscalco *et al.* are, therefore, a clear and direct evidence for large effects of d-d correlations in $CdCr_2Se_4$. The order of magnitude of the d bandwidth which can be inferred from the data (~ 0.5–1 eV) is much larger than the estimate of the intra-atomic Coulomb interaction (~ 10 eV), which justifies the narrow band limit used in the theoretical analysis.[1–5] It is also in good agreement with the value deduced from the red shift of the optical absorption edge, if one interprets it as the broadening of the d band in the ferromagnetic phase.

$CdCr_2Se_4$ is the first indisputable example of a new class of magnetic semiconductors in which the same electrons are responsible for both conduction and magnetism. It contrasts with the usual class of semiconductors in which conduction takes place in broad bands, coupled by exchange to localized $3d$ or $4f$ magnetic moments. This distinction is somewhat analogous to the distinction between transition metals in which magnetic properties are due to itinerant electrons in a d band and rare-earth metals in which magnetism is due to localized moments.

---

*Laboratoire associé au CNRS.

[1] M. Héritier, P. Lederer, and F. Brouers, in *Proceedings of the International Conference on Magnetism, Moscow, 1973* (Navka, Moscow, 1974), Vol. I, p. 181.

[2] M. Héritier and P. Lederer, Franco-British Centenary Conference, Jersey, 1974 (joint meeting of the Physical Society and Société Française de Physique) (unpublished).

[3] M. Héritier, thèse d'état (Université de Paris-Sud, Orsay,

1975) (unpublished).
[4]P. Lederer, F. Brouers, and M. Héritier, J. Phys. (Paris) 35, 171 (1974).
[5]D. Hone, P. Lederer, and M. Héritier, J. Phys. (Paris) 36, 1249 (1975).
[6]G. Harbeke and H. Pinch, Phys. Rev. Lett. 17, 1090 (1966).
[7]H. W. Lehman, Phys. Rev. 163, 488 (1967).
[8]C. Haas, Phys. Rev. 168, 531 (1968).
[9]T. Kasuya and A. Yanase, Rev. Mod. Phys. 40, 684 (1968).
[10]A. Yanase, Solid State Commun. 9, 2111 (1971).
[11]M. S. Erukhimov and S. G. Ovchinnikov, Fiz. Tverd. Tela (Leningrad) 21, 351 (1979) [Sov. Phys. Solid State 21, 209 (1979)].
[12]I. Balberg and M. D. Coutinho-Filho, J. Appl. Phys. 50, 1920 (1979).
[13]A. Selmi, P. Gibart, L. Goldstein, and A. Tomas, Jpn. J. Appl. Phys. 19, 267 (1980).
[14]A. Selmi, thése de troisième cycle (Université Paris VI, 1979) (unpublished).
[15]M. Héritier and P. Lederer, J. Phys. (Paris) Colloq. 41, C5-93 (1980).
[16]I. Balberg and A. Maman, Phys. Rev. B 16, 4535 (1977).
[17]P. Lederer, M. Héritier, and F. Brouers, Solid State Commun. 11, 1759 (1972).
[18]A. Selmi and M. Héritier (unpublished).
[19]W. J. Miniscalco, B. C. McCollum, N. G. Stoffel, and G. Margaritondo, Phys. Rev. B 25, 2947 (1982).