Comment on "Revised Fine Splitting of Excitons in Diamond"

Sauer *et al.* report in [1] on the exciton fine structure of diamond. Extending earlier work on *bound* excitons [2,3], they observe the same fine structure (two groups of spectral features, separated by about 11 meV, with four lines each) for the *free* excitons [4]. Sauer *et al.* suggest *"a novel coupling scheme of electrons and holes into excitons applying specifically to diamond."* They propose that exchange interaction dominates in both diamond excitons and spin-orbit coupling plays a minor role, only to the extent of introducing a level mixing that makes both groups of the fine structure, spin singlet and triplet, optically allowed (the triplet would not be allowed for pure exchange coupling). However, only qualitative arguments are given to support this interpretation.

Here we quantitatively determine the, by no means negligible, spin-orbit splitting of the edge excitons in diamond and the smaller exchange parameter from the *level splitting* between the two groups of lines [1,2], and their *spectral weights*, estimated from Fig. 1 of Sauer *et al.* We further show that these results for diamond are in good agreement with those obtained by scaling [5] known parameters for other semiconductors and, in the case of the spin-orbit splitting, with recent band-structure-based calculations [6].

The relative importance of spin-orbit coupling λ and exchange interaction Δ in excitons has been treated extensively [7,8]. In the simple case of coupled excitons involving the hole states $|J = 1/2, J_z = \pm 1/2\rangle$ and $|J = 3/2, J_z = \pm 1/2\rangle$ of diamond, analytical expressions can be derived [7]. While the energy level splitting $E_A - E_C$ of the two interacting states is rather insensitive to Δ/λ, their relative spectral weight I_C/I_A varies very strongly with the ratio of the two interactions [7] (e.g., for $\Delta/\lambda \simeq 2, I_C/I_A \simeq 10$). This theory has also been used [9] to explain the details of the exciton doublet observed in the partial photoemission yield spectrum of the Al $2p$ core exciton in AlSb.

In addition to the level splitting of about $E_A - E_C = 11$ meV observed for the edge exciton in diamond [1,2] (notation of Ref. [7]), the data of Sauer *et al.* (dotted curves in their Fig. 1) show that the intensities of the two doublet components are essentially the same, i.e., $I_C/I_A = 1$. From these values, using Eqs. (2.9) and (2.10) of Ref. [7], we obtain $\lambda = 11.7$ meV and $\Delta = 3.9$ meV. λ is very close to the value of 13 meV obtained in a recent band calculation [10]. The difference between 11.7 and 13 meV reflects the reduction in spin-orbit splitting for acceptor levels discussed in [6]. These results show that the exchange interaction, albeit sizable, hardly influences the energy level splitting. However, the intensity ratio of the emission is strongly affected.

In order to highlight the general nature of our results, we show in Table I the exchange splittings $\tilde{\Delta}$ for several semiconductors estimated with the expression proposed in [5] for materials with direct gaps <2 eV:

$$\tilde{\Delta} = 15.4 \times 10^3 a_{ex}^{-3} \text{ meV} \quad (1)$$

(a_{ex} is the exciton Bohr radius in angstroms). To demonstrate that this expression can be extrapolated to larger and indirect gaps [11] we compare in Table I the $\tilde{\Delta}$ obtained with Eq. (1) with experimental data for ZnSe, CuCl (direct gap), and GaP (indirect). Table I also includes the value of 3.9 meV, found with Eq. (1) for diamond. It is the same as extracted by us from the data of Sauer *et al.*

TABLE I. Exchange couplings $\tilde{\Delta}$ from Eq. (1) compared to experimental values (Δ).

	a_{ex} [Å]	$\tilde{\Delta}$	Δ [meV]
ZnSe	40.5	0.23	0.45[a]
GaP	31	0.52	0.5[a]
C	15.8	3.90	3.9[b]
CuCl	10.1	14.95	10.8[a]

[a]Ref. [12].
[b]extracted from the data in [1] as described in the text.

In conclusion, the exchange and spin-orbit interactions in diamond follow the general trend for tetrahedral semiconductors. The spin-orbit splitting is larger than the exchange splitting but somewhat smaller than that at the band edge, in agreement with [6].

M. Cardona, T. Ruf, and J. Serrano
Max-Planck-Institut für Festkörperforschung,
Heisenbergstrasse 1
D-70569 Stuttgart, Germany

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[1] R. Sauer *et al.,* Phys. Rev. Lett. **84**, 4172 (2000).
[2] H. Sternschulte *et al.,* Mater. Sci. Forum **258**, 1113 (1997).
[3] S. J. Sharp *et al.,* J. Phys. Condens. Matter **9**, L451 (1997).
[4] An essential part of Ref. [1] was published in Ref. [2].
[5] H. Fu *et al.,* Phys. Rev. B **59**, 5568 (1999).
[6] J. Serrano *et al.,* Solid State Commun. **113**, 411 (2000).
[7] Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **22**, 833 (1967).
[8] K. Cho, *Excitons* (Springer, Heidelberg, 1979), p. 23.
[9] R.L. Johnson *et al.,* in *Proceedings of the International Conference on the Physics of Semiconductors,* edited by D.J. Chadi and W.A. Harrison, (Springer, New York, 1985), p. 1239.
[10] M. Willatzen *et al.,* Phys. Rev. B **50**, 18 054 (1994).
[11] M.M. Denisov and V.P. Makarov, Phys. Status Solidi (b) **56**, 9 (1973).
[12] *Numerical Data and Functional Relationships in Science and Technology,* edited by O. Madelung, Landolt-Börnstein Series III, Vols. 17a, 17b, 22a, and 41b (Springer, Berlin, 1999).

