Reply to a comment on the electronic structure of nickel

Leonard Kleinman
Department of Physics, University of Texas, Austin, Texas 78712
(Received 2 June 1980)

Treglia, Ducastelle, and Spanjaard (TDS) have pointed out that we neglected a large term of opposite sign to the one we considered in our calculation of the reduction of the exchange splitting in Ni due to correlation. We show that this term does not affect our conclusions and that TDS's comment that the ratio of the self-energy of majority-spin to minority-spin electrons is 5/4 is not correct.

We[1] have recently pointed out that there are differences between the majority- and minority-spin-correlation energies in Ni which cannot be accounted for within the von Barth–Hedin[2] exchange-correlation potential which is based on a free-electron-gas approximation. In particular, we showed that one term, involving the scattering of a d electron by another d electron into two empty d states, occurs only for minority-spin electrons and should be large enough to account for the difference between the calculated[3] exchange-correlation splitting and the experimental value.[4] The self-energy of an electron consists of its correlation energy minus the correlation energy of the hole it leaves behind when photoemitted. Treglia, Ducastelle, and Spanjaard[5] (TDS) pointed out that we neglected the latter term, that it is larger than the term we considered and of opposite sign, and thus strongly implied that our conclusions were incorrect. Aside from a comment that in the ferromagnetic case $\Sigma_\uparrow/\Sigma_\downarrow=\frac{5}{4}$, where $\Sigma_\downarrow$ and $\Sigma_\uparrow$ are majority- and minority-spin self-energies, TDS considered paramagnetic Ni only. It is the purpose of this note to show that the hole term also serves to reduce the exchange-correlation splitting at the top of the d bands,[6] that $\Sigma_\uparrow/\Sigma_\downarrow\neq\frac{5}{4}$, and that the conclusions of Ref. 1 stand.

After dropping the factor 2 in the first term of Eq. (A4) which arose from a double counting of the parallel-spin intermediate states (Feyman diagrams also indicate the 2 is incorrect[7]) and including the hole term, Eq. (1) of Ref. 1 becomes

$$\Sigma_\sigma=-[0.032n_\sigma(5-n_\sigma)^2+0.040n_{\bar\sigma}(5-n_{\bar\sigma})(5-n_\sigma)]U^2/\epsilon_e+[0.032(5-n_\sigma)n_\sigma^2+0.040(5-n_{\bar\sigma})n_{\bar\sigma}n_\sigma]U^2/\epsilon_h\,.$$

Here ϵ_e is an average energy to excite the electron of interest and some other electron into two empty states, and ϵ_h is the average energy to excite some electron into an empty state and another electron into the hole left behind by the photoemitted electron. When the electron is at the top of the d bands, $\epsilon_e=\frac{1}{2}W$ and $\epsilon_h=W$, where W is the bandwidth. Taking $n_\sigma=5$, $n_{\bar\sigma}=4.4$, and $W=4.6$ eV, we find $\Sigma_\uparrow=0.115U^2$ eV, while taking $n_\sigma=4.4$ and $n_{\bar\sigma}=5$ yields $\Sigma_\downarrow=0.059U^2$ eV. Thus correlation reduces the exchange gap by $0.056U^2$ eV and it requires a value of $U=3.2$ eV to reduce the calculated[3] Kohn-Sham exchange splitting, 0.88 eV, to the experimental value, 0.31 eV.

For an electron at the bottom of the d bands, $\epsilon_e=1.5\,W$ but it is not possible to estimate ϵ_h because the two contributions to the energy denominator have opposite signs, making ϵ_h^{-1} an average of very large quantities of opposite sign. TDS nevertheless find Σ is negative at the bottom of the bands while agreeing with our result here that it is positive at the top of the bands. It is ironic, since it is generally believed that many-body effects reduce the d-band width of Ni, that second-order perturbation theory indicates the opposite result.

This work was supported by the National Science Foundation under Grant No. DMR 77-21559.

[1]L. Kleinman, Phys. Rev. B 19, 1295 (1979).
[2]U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).
[3]C. S. Wang and J. Callaway, Phys. Rev. B 15, 298 (1977).
[4]D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. 40, 1514 (1978).
[5]G. Treglia, F. Ducastelle, and D. Spanjaard, Phys. Rev. B 21, 3729 (1980).
[6]Whereas the electron term gives a negative self-energy to the minority-spin electrons, the hole term gives a positive self-energy to both spins but it is larger for the majority spins.
[7]A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971). It is obvious that the contribution of the third diagram of Fig. 11.5 is independent of the spin of the electron-hole pair. The fourth diagram cancels the third for identical orbitals with parallel spin leading to the condition $\alpha\neq\beta$ in the first sum in Eq. (A4) of Ref. 1.

