[5] V. L. Moruzzi, J. F. Janak, A. R. Williams, *Calculated Electronic Properties of Metals*, Pergamon, New York, **1978**.
[6] E. Müller-Hartmann, *J. Low Temp. Phys.* **1995**, *99*, 349.
[7] G. Stollhoff, P. Thalmeier, *Z. Physik B* **1981**, *43*, 13.
[8] A. M. Oleś, G. Stollhoff, *Phys. Rev. B* **1984**, *29*, 314.
[9] G. Stollhoff, *Phys. Rev. B* **1998**, *58*, 9826.
[10] G. Stollhoff, *Europhys. Lett.* **1995**, *30*, 99.
[11] D. van der Marel, G. A. Sawatzky, *Phys. Rev. B* **1988**, *37*, 10674.
[12] A. Liebsch, *Phys. Rev. Lett.* **1979**, *43*, 1431.
[13] P. Unger, J. Igarashi, P. Fulde, *Phys. Rev. B* **1994**, *50*, 10485.
[14] M. I. Katsnelson and A. I. Lichtenstein, *J. Phys. Condens. Matter* **1999**, *11*, 1037.
[15] G. Stollhoff, *Europhys. Lett.* **1995**, *29*, 463.
[16] D. Vollhardt, N. Blumer, K. Held, M. Kollar, J. Schlipf, M. Ulmke, J. Wahle, *Adv. Solid State Phys.* **1999**, *38*, 383.
[17] J. Bünemann, W. Weber, F. Gebhard, *Phys. Rev. B* **1998**, *57*, 6896.
[18] G. Stollhoff, unpublished results.
[19] C. Herring in *Magnetism*, *Vol. 4* (Eds.: G. Rado, H. Suhl), Academic Press, New York, **1966**.
[20] G. Stollhoff, A. M. Oleś, V. Heine, *Phys. Rev. B* **1990**, *41*, 7028.
[21] G. Stollhoff, *J. Magn. Magn. Mater.* **1986**, *54–57*, 1043.
[22] A. M. Oles, G. Stollhoff, *Europhys. Lett.* **1988**, *5*, 175.
[23] G. Stollhoff, A. M. Oleś, V. Heine, *Phys. Rev. Lett.* **1996**, *76*, 855.
[24] R. Pardon, J. Gräfenstein, G. Stollhoff, *Phys. Rev. B* **1995**, *51*, 10556.

Reply

Gregory A. Landrum and Richard Dronskowski*

In the preceding paper,[1] many-body theorist Gernot Stollhoff criticizes our recent review of a chemistry-oriented approach to understanding metallic ferromagnetism.[2] Although we heartily welcome a lively debate between chemists and physicists on the subject, Stollhoff's critique, in our view, misses the deciding point.

Within the largest part of his text, Stollhoff goes to great lengths to speak in favor of the Hubbard ansatz and related theories based on $W/J/U$ parameters. He also presents his own mini review explaining ferromagnetism in metallic species. For an, admittedly quite concise, treatment of Hubbard models, the reader is referred to Sections 2.3, 3.1, and especially 5.1 of our review.[2] As we have already said, Stollhoff's theoretical approach is far from being the only theory in existence. Stollhoff questions both density functional theory (DFT) as well as the local density approximation (LDA), and promotes his own computational approach. Stollhoff obviously has severe problems with accepting DFT in general, but that is another matter. With respect to our own theory, we do not demand that the method we are using to construct chemical explanations be 100 percent "accurate" (whatever that means) although the LDA is, as he admits, totally precise in its predictions with respect to ferromagnetism and the transition metals.

It is true that our results are based on density functional (mostly LDA) calculations; while the LDA performs astonishingly well in most cases, there are deficiencies that we summarized in Sections 5.2 and A.1. Two years ago an independent review on the successes and failures of DFT was presented from the perspective of the physics community.[3] However, the presence of antibonding states at the Fermi level is observed, which we view as the ferromagnetic "fingerprint", in *both* LDA and gradient corrected calculations (see Section A.1)! This much at least is not an artifact of the LDA. It was not in fact our intention to "sell" DFT or LDA or any other numerical theory as the optimum solution. On the contrary, as we demonstrated in Appendix B, a much more primitive theory, the extended Hückel (!) is able to reproduce the ferromagnetic fingerprint, provided that the method is asked the right questions. Thus, we have demonstrated that the characteristic effect is theoretically "good-natured" and does not need an excessively sophisticated treatment. Also, our approach is orbital oriented and may thus be easily subjected to a chemical interpretation. It is hard for us to say whether equations (1)–(6) of Stollhoff's article[1] contain chemically valuable information, and we leave this decision to the experimentalists.

Towards the end Stollhoff touches our contribution directly. When talking about fcc- and bcc-Fe, Stollhoff actually uses our results but does not present new information. With respect to his discussion of Co and Ni, he does not consider the changing position of the Fermi energy within the fcc density of states since our explanation allows more immediate insight than his $W/J/U$ reasoning. In fact, the crystal-orbital Hamilton population (COHP) result in Figure 21 of ref. [2] qualitatively demonstrates the different strengths of ferromagnetism in Fe, Co, and Ni! Concerning Stollhoff's remarks on the heavier transition metals, he does not realize the analogy between main group and transition metal chemistry as far as differential shielding is concerned. He writes about the situation with Pd and Pt: "The origin of the decrease of the J is, by the way, not a result of stronger screening but because the 4d and 5d atomic orbitals are more diffuse (a consequence of the enlarged core)." Exactly, the 4d and 5d atomic orbitals are more diffuse, and the core is enlarged. This was the basis of our argument. We did not attempt to explain the decrease of J, we wanted to avoid any mention whatsoever of J in our treatment of the heavier transition metals.

On the other hand, Stollhoff does not seem to understand the origin of the negative COHP at the Fermi energy although

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we have pictorially indicated its origin from the t_{2g} orbitals in Figures 14 and 16 of ref. [2]. The message contained in Stollhoff's remark "The negative energies of the local 3d COHPs have nothing to do with magnetism itself. In my opinion, they might be connected to the charge transfer from the 4s,4p orbitals to 3d." is not clear to us. Continuing his criticism of COHPs Stollhoff says: "There is no need for seemingly new information like the COHP of LD in the context of itinerant ferromagnetism." This type of statement is indefensible in any scientific paper. While interpretive tools apparently hold no value within some segments of community A, they can be well received by a significant portion of community B. Each community develops its own complexity of questions and answers. Stollhoff: "…the narrowing of the majority band and the widening of the minority band do not cause ferromagnetism but instead represent an attempt to reduce a little the band-energy losses originating from the ferromagnetic redistribution…" The changes in band width are, as we write in our review, a consequence of ferromagnetism. We do *not* call them a cause. We fail to see, however, how narrowing a band can *reduce* kinetic energy penalties. Unless our own understanding is also hampered by language barriers, broadening the minority band certainly helps out on the kinetic energy front, but narrowing the majority band results in a kinetic energy penalty.

Summarizing, a many-body theorist is arguing in favor of his method. There is nothing to say against such work, at least as long as it allows new insight and does not unnecessarily disparage other approaches. At the same time, we believe that we have the right to argue in terms of our own theory of ferromagnetism which is not only in harmony with atomic and molecular findings but can also, as we have shown, be extended to intermetallic alloys. Let us remind the reader that the purpose of our work was not to present the one, true, eternal theory of ferromagnetism, but to provide a framework by which the phenomenon could be more easily grasped by chemists and, more importantly, be used to help guide synthetic attempts. We again note that our qualitative picture is conceptually straightforward and can be used productively: Want to increase the chances of an alloy being ferromagnetic? Increase or decrease the electron concentration to shift the Fermi energy towards those antibonding states at the top of the d block. It is probably much harder to see how to increase the Hubbard J value of a complicated alloy. Besides that, our theory is in excellent harmony with other chemical ideas such as the concept of chemical hardness, which now turns out to be a quantitative ferromagnetism criterion.

We acknowledge that it perhaps costs efforts for some colleagues to accept or at least understand our chemical theory of metallic ferromagnetism since it does not rely on the standard physics arguments. In fact, there are a number of good reasons not to follow that typical reductionist approach.[4] On the contrary, our approach is just another demonstration that the atoms/bonds paradigm does have its justification in the quantum world, especially if it allows a simple, chemical, but still precise picture of itinerant ferromagnetism. From this perspective, our finding seems to be chemically obvious although it has been overlooked by many for a very long time because of their reductionist point of view. Finally, we believe that there is another lesson to be learned: We certainly need more bridges between theoretical physics and chemistry. Theoretical chemists have profited enormously, and still do, from solid-state quantum physics in the last two decades, and we only hope that some of our many-body friends will read more chemical journals and learn more about theoretical chemistry ideas. Stollhoff's contribution demonstrates that the first part of that has happened, and that is a start.

[1] G. Stollhoff, *Angew. Chem.* **2000**, *112*, 4643; *Angew. Chem. Int. Ed.* **2000**, *39*, 4471.

[2] G. A. Landrum, R. Dronskowski, *Angew. Chem.* **2000**, *112*, 1598; *Angew. Chem. Int. Ed.* **2000**, *39*, 1560.

[3] L. Fritsche, B. Weimert, *Phys. Status Solidi B* **1998**, *208*, 287.

[4] R. Hoffmann, *The same and not the same*, Columbia University Press, New York, **1995**, p. 18.