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What density-functional theory can tell us about the spin-density wave in Cr

S Cottenier[1], B De Vries[1], J Meersschaut[1,2] and M Rots[1]

[1] Instituut voor Kern- en Stralingsfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium
[2] Argonne National Laboratory, 9700 S Cass. Avenue, Argonne, IL 60439, USA

E-mail: stefaan.cottenier@fys.kuleuven.ac.be

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Abstract

The energy-versus-volume curve of the spin-density wave (SDW) in body-centred-cubic Cr is calculated with the density functional theory/full-potential linearized augmented plane wave (DFT/FLAPW) method using the generalized gradient approximation (GGA). The predicted ground state is not the SDW, in contrast to an earlier FLAPW calculation. A conjecture is formulated that the widely varying results of the local density approximation (LDA) and GGA—and of different solution methods—can be scaled by the size of the calculated moment. As a consequence, experimentally relevant properties of the SDW can be calculated by tuning the moment. The implications of these results for the ability of DFT to describe Cr are discussed.

1. Introduction

Although it has a simple crystallographic structure and contains only one element, body-centred-cubic (bcc) Cr keeps triggering experimental and theoretical work. The reason is its peculiar magnetic ground state: an incommensurate antiferromagnetic (AF) spin-density wave (SDW), which originates from nesting properties of the Fermi surface (see [1] for reviews). During the past 20 years, most of the theoretical work on Cr has been done in the framework of density functional theory (DFT), using both the local density approximation (LDA) and generalized gradient approximation (GGA) [2–18]. None of these studies has succeeded in giving a really satisfying description of Cr. Doubts have even been raised [17] as to whether DFT is able to yield an SDW at all as the ground state for Cr. In this paper, we present the first GGA energy-versus-volume minimization in the SDW state. This result combined with the above-mentioned studies offers a clear picture of the systematics in DFT/LDA–GGA predictions for Cr. It will be shown that neither LDA nor GGA captures the right physics for ground state considerations, but we shall show how both nevertheless can be used for reliably describing the magnetism of Cr.

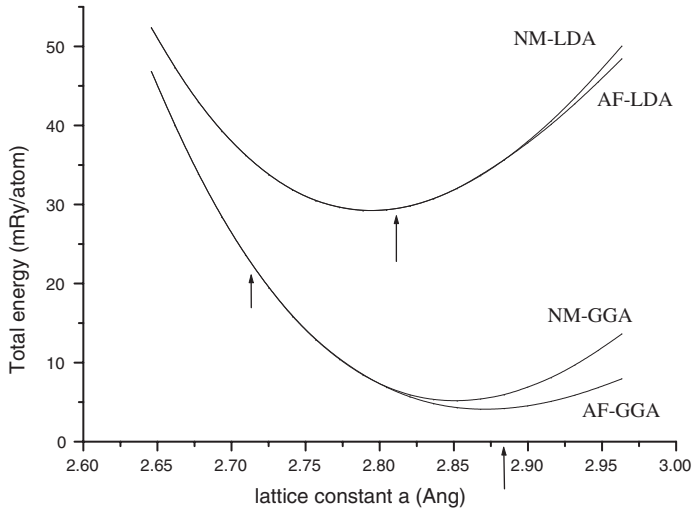

Figure 1. Total energy as a function of lattice constant for NM and AF Cr, calculated by LDA and GGA. The energy axis has an arbitrary zero-point. The LDA and GGA curves are vertically shifted over an arbitrary amount with respect to each other. The curves shown are Murnaghan fits, obtained by 21 points for each curve. No scatter at all was present. Vertical arrows indicate the branching point of the AF curve and the experimental lattice constant $a_{\mathrm{SDW}}^{\mathrm{exp}}$.

2. A survey of the literature

Although the SDW is the ground state in nature, computational convenience has made the closely related AF state the theoretically most studied. Comparing several LDA [2–8, 11–13] and GGA [9, 14–18] studies for the AF and nonmagnetic (NM) states, the following general picture emerges. The NM and AF energy-versus-volume curves behave qualitatively similarly in LDA and GGA (figure 1): at low volumes, the magnetic moment is quenched and the two curves are identical. At a given volume the moment appears and the AF curve splits off from the NM curve, the former being at lower energy. An important difference between LDA and GGA is the position of this branching volume. For LDA it lies to the right of the total-energy minimum [8, 11]; for GGA it lies to the left of it [14]. The numbers obtained for the NM and AF equilibrium volume and for the bulk modulus cannot be compared with experiment directly, as the experimental ground state is the SDW. The NM LDA volume is a few per cent lower than $V_{\mathrm{SDW}}^{\mathrm{exp}}$ ($V_{\mathrm{SDW}}^{\mathrm{exp}} = (a_{\mathrm{SDW}}^{\mathrm{exp}})^3 =$ the experimental volume in the SDW state). The GGA NM volume lies between the LDA NM volume and $V_{\mathrm{SDW}}^{\mathrm{exp}}$, while the GGA AF volume almost coincides with $V_{\mathrm{SDW}}^{\mathrm{exp}}$. The NM bulk modulus both for LDA and GGA is larger than the experimental SDW value, the AF GGA bulk modulus is comparable to the latter. At the experimental lattice constant, the LDA AF moment matches the experimental amplitude of the SDW. The GGA AF moment is twice as high. Also at the AF equilibrium volume, the AF moment is much higher compared with experiment.

Starting with the Korringa–Kohn–Rostoker (KKR) LDA work of Hirai [10, 12], a few studies applying static DFT to the SDW state have been published [15–18]. Hirai finds an SDW with the experimental period of about 20 lattice constants to be slightly (0.011 mRyd/atom) lower in energy than the AF state (see [12] and reference 22 in [17]). Its amplitude is 0.67 μ_{B} at the experimental lattice constant. The SDW solution branches off earlier than the AF curve does, but still to the right of the NM minimum. The latter therefore remains the predicted

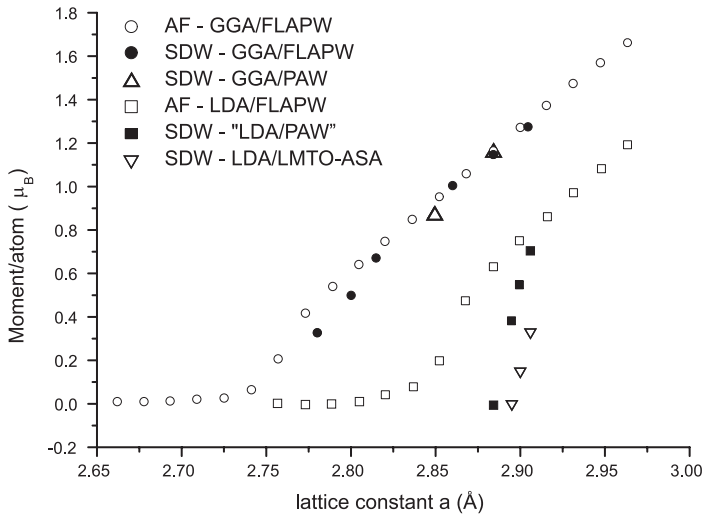

Figure 2. Magnetic moment (μ_B) as a function of lattice constant (Å) for a simple AF cell with GGA/FLAPW and LDA/FLAPW (both this work), for the SDW with $p = 20$ using GGA/FLAPW (this work) and GGA/PAW (see [17]) and for the SDW using LDA/LMTO-ASA (see [17]) and an estimate for LDA/PAW based on the latter data.

ground state. In the region where the SDW exists but the AF state does not, the amplitude of the SDW is remarkably high ($\sim$0.4 μ_B), especially when considering the small energy gain [17]. The LDA/LMTO-ASA (linearized muffin-tin orbital method with atomic sphere approximation) study from Hafner *et al* [17] led to a quite different conclusion. An SDW with the experimental period is possible only from a lattice constant $a = 2.895$ Å onwards (figure 2; see further for discussion). Extrapolation suggests that it reaches the experimental amplitude at about $a_0 = 2.916$ Å, and lies then 0.20 mRyd/atom *higher* in energy than the AF state. Although it is not clear why the two studies yield different results[3], they show that with LDA the SDW cannot be found as the ground state.

When GGA is used with both LMTO-ASA ($a = 2.884$ Å, fixed) and the projector augmented wave (PAW) method ($a = 2.849$ Å, fixed), an SDW can be obtained for a wide range of periods of the wave [17, 18]. For all periods, the AF state is lower in energy than the SDW, in contrast to a limited GGA/FLAPW study [15] that found an SDW with a period of 14 unit cells and $a = 2.85$ Å to be lower in energy than AF (figure 3). This contradiction is remarkable: PAW and FLAPW are both highly accurate methods and should, at the same lattice constant, yield comparable results. All GGA studies confirm the greatly overestimated amplitude of the SDW.

3. Method

All calculations in this work were made using the WIEN implementation [19] of the full-potential linearized augmented plane wave (FLAPW) method. The LDA [20] and GGA [21] functionals from Perdew *et al* are used (for the SDW only GGA). In the FLAPW procedure wavefunctions, charge density and potential are expanded in spherical harmonics within nonoverlapping atomic spheres of radius R_{mt} and in plane waves in the remaining space

[3] We can mention here also that we were not able to obtain an SDW with LDA/FLAPW at the experimental lattice constant.

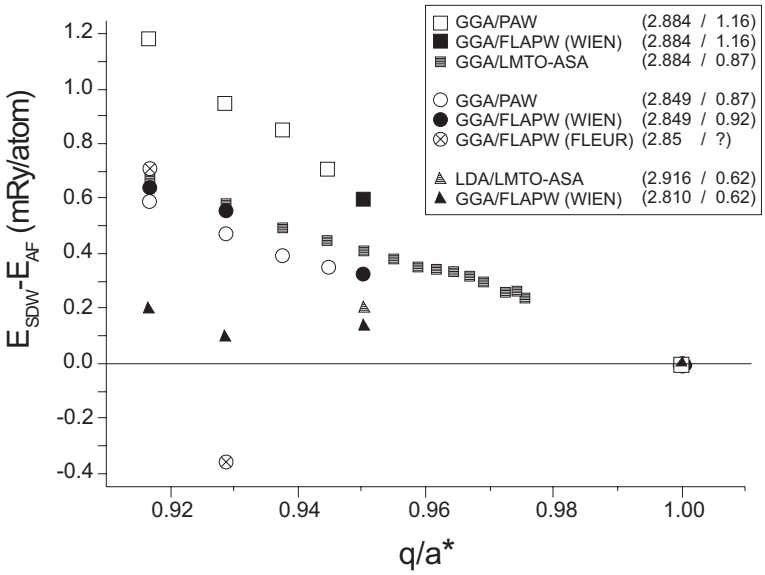

Figure 3. $E_{\mathrm{SDW}} - E_{\mathrm{AF}}$ (mRyd/atom) as a function of the reduced wavevector $q/(a/2\pi) = (1-p)/p$, with p the period expressed in number of AF lattice constants. White symbols: PAW. Black symbols: FLAPW (WIEN). Gray symbols: LMTO-ASA. ⊗: FLAPW (FLEUR). Squares are used if the lattice constant is the experimental one, circles if it is the equilibrium GGA value and triangles if the moment is tuned to the experimental moment. The legend lists the lattice constant (Å) and the moment at $p = 20$.

of the unit cell. The maximum multipolarity l for the waves inside the atomic spheres was confined to $l_{\max} = 10$. The wavefunctions in the interstitial region were expanded in plane waves with a cutoff of $k_{\max} = 9/R_{\mathrm{mt}}$ for the NM and AF calculations, and $k_{\max} = 8/R_{\mathrm{mt}}$ for the SDW cases. The muffin-tin radius R_{mt} was 2.1 au for the NM and AF cases with small unit cells and 2.25 au for supercells, the latter to keep the calculation time reasonable (smaller R_{mt} are slightly more accurate, but much more expensive). For internal consistency, moments obtained with $R_{\mathrm{mt}} = 2.25$ au were rescaled to moments with $R_{\mathrm{mt}} = 2.1$ au. The rescaling relation was obtained by means of an extra series of AF calculations with $R_{\mathrm{mt}} = 2.25$ au, in the range of 2.74–2.95 Å. For the same reason and by the same procedure, total energies were corrected. The validity of both corrections—which do not qualitatively change any of our conclusions, but contribute to the quantitative consistency of the results—was checked by a direct calculation of an AF and an SDW supercell using $R_{\mathrm{mt}} = 2.1$ au at $a = 2.78$ Å, and the agreement was excellent. The charge density was Fourier expanded up to $G_{\max} = 16$. A mesh of 220 special k-points was taken in the irreducible wedge of the Brillouin zone for the NM and AF cases; 36 special k-points were used for the supercell calculations. Because of the small energy differences involved and the large range of lattice constants studied, it was crucial to deal with the linearization energies properly. For a preliminary series of AF calculations, the linearization energies were determined from the density of states (DOS) as a function of volume. This yielded smooth functions, which were then used to run all calculations reported below with the optimal linearization energies for that volume. No spin–orbit coupling was taken into account. These calculations are therefore not sensitive to the polarization (transversal or longitudinal) of the SDW.

Table 1. High-precision FLAPW results using LDA and GGA for the NM and AF state, and using GGA for the SDW. For NM and AF, the numbers are taken from a Murnaghan fit through nine points in the volume region ±10% of the equilibrium, where the Murnaghan equation is valid. Tabulated are the lattice constant in the NM and AF states (a_0 [Å]), bulk modulus in the NM and AF states (B [GPa]), magnetic moment per atom at the experimental lattice constant and at the calculated AF lattice constant [μ_B] and the lattice constant a_{split} at which the magnetic curve branches off from the NM one [Å]. This branching happens asymptotically; the reported a_{split} is the point at which the moment exceeds 0.02 μ_B. The moment is defined within a sphere with radius $R_{mt} = 2.1$ au for the NM and AF calculations, and corrected to the same sphere for the SDW. For the waves, the moment is the amplitude. $^{(*)}$ = extrapolated.

	a_0 (NM)	a_0 (AF)	B (NM)	B (AF)	μ (a_0^{exp})	μ (a_0^{theo})	a_{split}
LDA	2.794		308		0.63		2.81
GGA	2.851	2.871	260	184	1.16	1.08	2.71
SDW-GGA		2.865		217	1.15	1.04	$2.76^{(*)}$
SDW-exp		2.881		191	0.62		

4. Results

For present-day computers, NM and AF Cr (one and two atoms per unit cell, respectively) are easy systems to calculate. The numerical accuracy can therefore be pushed to high limits. In figures 1 and 2 and in table 1 we present total energies, magnetic moments and lattice constants, obtained from FLAPW calculations with settings described above. For the sake of numerical comparison, the NM and AF unit cells were both taken to contain two atoms. These results can be considered to be the 'true' LDA and GGA results, without numerical inaccuracies, and they are in good agreement with recent values obtained by PAW [17] and an independent FLAPW implementation [15]. For the SDW, we use a supercell of dimensions $(a,\ a,\ 20\,a)$ (a is a bcc Cr lattice constant), which is close to the observed period of the SDW (20.83 a). First we check our supercell calculations against other methods. Figure 3 shows the energy difference $E_{SDW} - E_{AF}$ for different values of the reduced wavevector q/a^* ($p = 1/(1-q/a^*)$ with p the period in bcc lattice constants, q is the wavevector of the SDW and $a^* = 2\pi/a$) obtained with GGA/FLAPW (FLEUR implementation) [15] and GGA/PAW [17, 18]. Both for $a = 2.884$ Å (squares) and $a = 2.849$ Å (circles) there is excellent agreement between the PAW data (white) and our FLAPW results (black), even on this mRy/atom scale (the deviating values [17] of the less accurate LMTO-ASA method will be discussed below). Also the FLEUR-FLAPW point at $q/a^* = 0.917$ is in good agreement, the one at $q/a^* = 0.292$ that favours the SDW is not. Because it can now be excluded that this is due to the FLAPW method, we can strengthen the conclusion of Hafner *et al* that the latter point is erroneous, and we show that there is no contradiction between PAW and FLAPW.

Figure 4 shows the total energy (mRyd/atom) for the AF, NM and SDW states as a function of lattice constant. The AF and NM are not directly the ones obtained in figure 1: due to systematic numerical errors, the total energy of an $(a,\ a,\ 20\,a)$ AF supercell is never exactly equal to 20 times the total energy of a two-atom AF cell, but is shifted over a small constant amount. In order to compare total energies, calculations must always be performed in identical circumstances. Therefore we calculated two AF supercells at $a = 2.815$ and 2.905 Å. After a rigid vertical shift, the AF curve from figure 1 nicely fits these points (figure 4). The total energy of the SDW supercells can now be directly compared with this curve. Four of these SDW supercells were calculated, and a Murnaghan equation of state was fitted (table 1 and figure 4). The energy difference $E_{SDW} - E_{AF}$ is shown in the inset of figure 4 (the curve is the

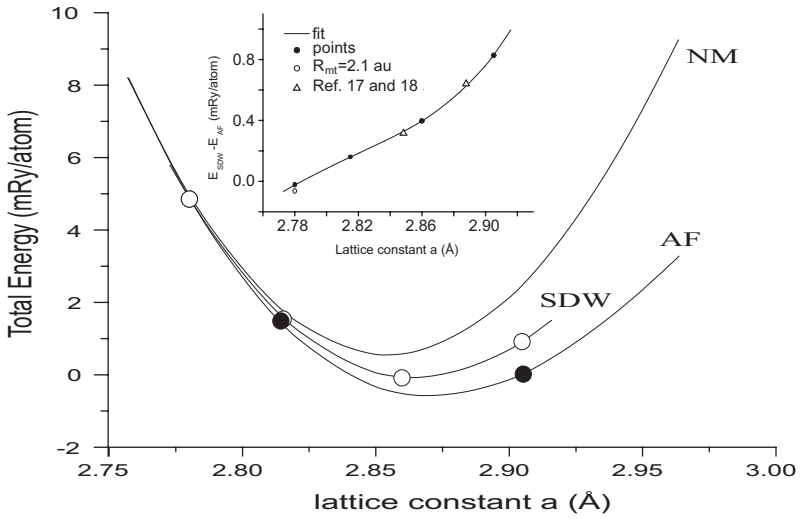

Figure 4. Total energy as a function of lattice constant for the NM, AF and SDW states. Inset: $E_{\mathrm{SDW}} - E_{\mathrm{AF}}$; the curve is the difference between the two Murnaghan fits. The two points of references [17] and [18] are in excellent correspondence.

difference between the SDW and AF Murnaghan fits). The energy of the SDW is intermediate between the AF and NM states, and over the complete volume range the AF energy is lowest. Also equilibrium volume and bulk modulus are intermediate between AF and NM, and agree rather well with experiment. The point at $a = 2.849$ Å is read from figure 3 in [17] and the one at $a = 2.884$ Å from figure 3 in [18]. They agree excellently with our results. The SDW Murnaghan fit is made down to $a = 2.78$ Å. For somewhat lower volumes the SDW will disappear and the total-energy curve must coincide with the NM, which in this volume region is very close to the AF state. The energy difference at $a = 2.78$ Å between SDW and AF supercells with $R_{\mathrm{mt}} = 2.1$ au is shown too. The small difference between this value and the value obtained after correction for $R_{\mathrm{mt}} = 2.25$ au can be taken as the error bar on our results.

The amplitude of the SDW is shown in figure 2, together with the GGA and LDA AF moment. Six instead of four SDW amplitudes are reported, including two cases with not the best linearization energies. This considerably affected the energies, but not the moments. The amplitude is almost equal to the AF moment for large volumes, and linearly decreases. Earlier than the AF moment does, the amplitude leaves the linear curve and drops to zero. Also here, the amplitude obtained in [17, 18] is in good agreement.

5. Discussion

As was mentioned above, the different predictions of LDA and GGA for Cr are two manifestations of what actually is a qualitatively very *similar* underlying behaviour. The similarity is even more striking than was shown so far. Hafner *et al* [17] present LDA/LMTO-ASA results for slightly expanded lattices, where an SDW with the experimental period appears to exist. The results from their figure 6 in reference [17] are given in figure 2. Their figure 1 shows how LDA/LMTO-ASA underestimates the AF moment with respect to LDA/PAW (an effect due to spherical averaging in the ASA). In figure 2 we use this information to estimate the corresponding amplitude of the better LDA/PAW SDW. This suggests that also the LDA SDW amplitude follows the AF moment, and then drops to zero earlier than the AF moment

does. There seems to be no fundamental difference between LDA and GGA: with GGA the same magnetic effects are visible as with LDA, but at lattice constants about 0.1 Å smaller.

A peculiar behaviour can be noticed when the SDW amplitude reaches its experimental value of 0.62 μ_B (at $a = 2.810$ Å for GGA). At this volume, the AF moment can be read from figure 2 to be slightly larger: 0.68 μ_B. This is in agreement with the somewhat enhanced experimental AF moment, which is 0.68 μ_B [22] or 0.66 μ_B [23]. The SDW is experimentally known to be almost sine-like, which means that in its Fourier expansion only the first term M_1 is very different from zero. The second term and all other even terms are zero by symmetry, and the third term M_3 gives the first order deviation from the sine shape. A negative M_3—or a negative ratio M_3/M_1—results in a slightly more 'rectangular' wave, while positive values yield a more 'triangular' wave. Higher order terms (M_5 and higher) are very small and essentially zero. The experimental value of M_3/M_1 is -0.016 or -0.021 [24]. In figure 5 (left axis), calculated values of this ratio are given as a function of lattice constant and the dahsed line indicates the experimental value. At $a = 2.810$ Å, the calculated ratio comes very close to experiment and is an order of magnitude better than the ratio obtained at $a_{SDW}^{exp} = 2.884$ Å. The SDW is known to be accompanied by a charge density wave (CDW), which has, due to symmetry, the odd terms equal to zero in its Fourier expansion. The only term appreciably different from zero is the second one, N_2, but the experimental value is not well known ($0.003 \rightarrow 0.02$, see reference [10]). The right scale of figure 5 shows N_2 as a function of lattice constant. At $a = 2.810$ Å, the calculated value has the right order of magnitude, and is two orders of magnitude closer to experiment than in previous calculations [10]. All this suggests that if the GGA amplitude is constrained to the experimental value, the calculated electronic structure comes close to the true situation. As a result, Cr with $a = 2.810$ Å can be used as a 'laboratory' to study the properties of the SDW with GGA. The tuned value of the lattice constant has no physical meaning and can be considered as a free parameter, set to a value that correctly reproduces magnetism. Working with this 'Cr laboratory' therefore means leaving the *ab initio* level of theory, and limits the kind of properties that can be studied.

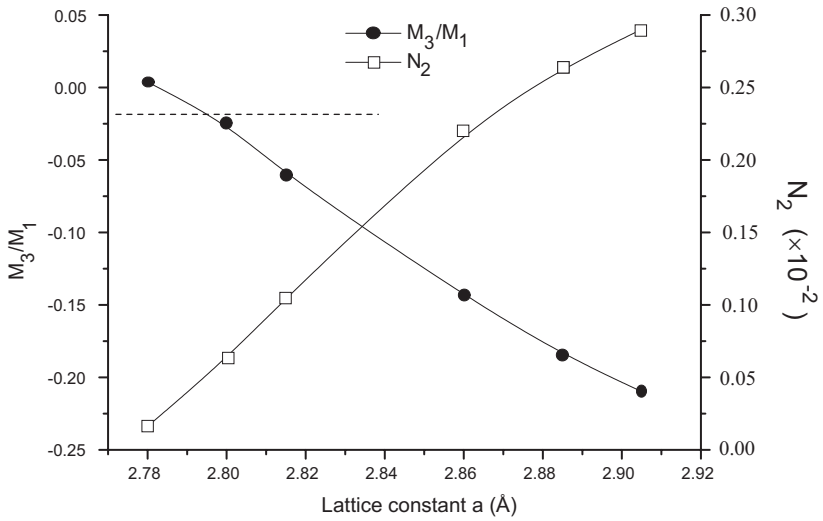

Figure 5. Left-hand scale: ratio between the third and first harmonics (M_3/M_1) of the SDW. Right-hand scale: the first nonzero (second) harmonic N_2 of the accompanying CDW. The horizontal line gives the experimental value of M_3/M_1.

This is a price that has to be paid, but probably an acceptable one: by setting only a single parameter, several different aspects of magnetic behaviour are coming out right. This suggests that enough predictive power is left, and that electronic structure insight obtained from this 'laboratory' will survive in the real world. We are currently using this approach to calculate hyperfine fields on impurities in SDW Cr.

We are now in the position to formulate the following Conjecture. *Across different approximations (LDA–GGA) and different methods (FLAPW, PAW, LMTO, . . .), the dominating factor in Cr is the size of the SDW amplitude. If scaled to the same moment, all approximations and methods yield the same behaviour.* Arguments for this conjecture are (1) the LDA–GGA similarity in figure 2. (2) The coincidence in figure 3 between the PAW-FLAPW results at $a = 2.849$ Å and the LMTO result at 2.884 Å which all have about the same moment at $q/a^* = 0.95$ (0.87 μ_B for PAW, 0.92 μ_B for FLAPW, 0.87 μ_B for LMTO). Even a method such as LMTO-ASA that is known to be less reliable—and therefore deviates from the energies found with PAW and FLAPW at $a = 2.884$ Å—yields energies that are identical to PAW and FLAPW in cases where they have the same moment. The moment rather than the lattice constant is the dominating factor. (3) The estimated $E_{SDW} - E_{AF}$ is 0.20 mRy/at from figure 5 in reference [17] at $a = 2.916$ Å, where LDA/LMTO-ASA should find the experimental amplitude. This estimate is indicated in figure 3 (gray triangle) and agrees with our corresponding GGA/FLAPW result (black triangle) at 2.810 Å (= the lattice constant where GGA/FLAPW finds the experimental amplitude with $p = 20$).

If it will survive new results obtained by other methods, a consequence of this conjecture would be that for every combination 'approximation/method' a lattice constant exists at which a realistic SDW is found. We showed this value to be 2.810 Å for GGA/FLAPW, and estimate it is similar for GGA/PAW, 2.905 Å for LDA/PAW and LDA/FLAPW and 2.916 Å for LDA/LMTO-ASA. Another consequence is of more fundamental importance. Hafner *et al* claim [17] that the final DFT answer for the ground state of Cr is AF (at least with LDA and GGA), which would need to invoke temperature and dynamics to understand the appearance of the SDW in nature. We believe this might be true, but it cannot be considered as proven yet. Due to the quantitative differences between LDA and GGA, and between the different methods, and regarding the small energy differences involved, more high-precision data are required. The magnetic moment conjecture provides a good tool for this: if for the experimental amplitude (tuned by the volume and at $p = 20$) the results of all approximations/methods bunch together around our value of 0.135 mRyd/atom in figure 3, the answer(s) of DFT can be said to be consistent and trustworthy. If in this way can be proven that the AF ground state is indeed the final LDA-GGA answer, two alternative conclusions can be drawn. Either DFT in its LDA or GGA formulation is not accurate enough to describe Cr. This would make Cr an ideal testing ground for improved exchange-correlation functionals: a newly proposed general-purpose exchange-correlation functional that claims to be better than LDA-GGA should reproduce LDA-GGA results there where they are correct, and improve on them where LDA-GGA fails, e.g. for Cr. Or alternatively, the LDA-GGA answer comes close to the true DFT result. Then dynamic features will be necessary to explain the Cr magnetism.

Finally, although GGA is a necessary extension in order to describe other 3d transition metals correctly, we want to stress that for Cr it cannot be decided whether GGA or LDA is superior. It is therefore dangerous to rely too heavily on features specific to for example LDA, as is done in the model of Marcus *et al* to understand the appearance of the SDW [8, 11]. Another warning is that it seems to be possible to make predictions about structural properties of Cr by using GGA (but then the magnetic moments do not make sense) *or* about magnetic properties in any approximation if the volume is well tuned. But if both the lattice and magnetism are involved (e.g. in magnetic Fe/Cr multilayers, where the Cr volume is determined by Fe) one

has to be extremely cautious. A careful treatment such as that used by Klautau *et al* [13] is needed then.

Acknowledgments

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References

[1] Fawcett E 1998 *Rev. Mod. Phys.* **60** 209
Fawcett E 1994 *Rev. Mod. Phys.* **66** 25
[2] Moruzzi V L, Williams A R and Frank J F 1978 *Calculating Electronic Properties of Metals* (New York: Pergamon) ch 5
[3] Kübler J 1980 *J. Magn. Magn. Mater.* **20** 277
[4] Skriver H L 1981 *J. Phys. F: Met. Phys.* **11** 97
[5] Kulikov N I and Kulatov E T 1982 *J. Phys. F: Met. Phys.* **12** 2291
[6] Kulikov N I, Alouani M, Khan M A and Magnitskaya M V 1987 *Phys. Rev.* B **36** 929
[7] Chen J, Singh D and Krakauer H 1988 *Phys. Rev.* B **38** 12 834
[8] Moruzzi V L and Marcus P M 1992 *Phys. Rev.* B **46** 3171
[9] Singh D J and Ashkenazi J 1992 *Phys. Rev.* B **46** 11 570
[10] Hirai K 1997 *J. Phys. Soc. Japan* **66** 560
[11] Marcus P M, Qiu S L and Moruzzi V L 1998 *J. Phys.: Condens. Matter* **10** 6541
[12] Hirai K 1998 *J. Phys. Soc. Japan* **67** 1776
[13] Klautau A B, Legoas S B, Muniz R B and Frota-Pessôa S 1999 *Phys. Rev.* B **60** 3421
[14] Guo G Y and Wang H H 2000 *Phys. Rev.* B **62** 5136
[15] Bihlmayer G, Asada T and Blügel S 2000 *Phys. Rev.* B **62** R11 937
[16] Schafer J, Rotenberg E, Kevan S D and Blaha P 2000 *Surf. Sci.* **454–6** 885
[17] Hafner R, Spišák D, Lorenz R and Hafner J 2001 *J. Phys.: Condens. Matter* **13** L239
[18] Hafner R, Spisak D, Lorenz R and Hafner J 2002 *J. Phys.: Condens. Matter* **14** 2119 (erratum)
[19] Blaha P, Schwarz K and Luitz J 1999 *WIEN97, a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties* (Vienna: Tech. Univ. Wien) ISBN: 3-95010310-4 (updated version of Blaha P, Schwarz K, Sorantin P and Trickey S B 1990 *Comput. Phys. Commun.* **59** 399)
[20] Perdew J P *et al* 1992 *Phys. Rev.* B **46** 6671
[21] Perdew J P, Burke S and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[22] Komura S, Hamaguchi Y and Kunitomi N 1967 *J. Phys. Soc. Japan* **23** 171
[23] Machida K and Fujita M 1984 *Phys. Rev.* B **30** 5284
[24] See references in reference [1]