Crystal structure of Ca(AlH$_4$)$_2$ predicted from density-functional band-structure calculations

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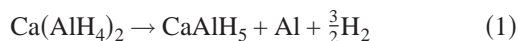(Received 18 January 2005; published 27 April 2005)

Calcium alanate $[Ca(AlH_4)_2]$ is a candidate material for high-density reversible solid-state hydrogen storage that thus far has been scarcely studied. This paper presents a scheme for solving the crystal structure of a compound based on only a few model structures from similar compounds and employs this to predict the crystal structure and electronic structure of $Ca(AlH_4)_2$. By deliberately breaking the symmetry of the model structures down to $P1$, local minima may be avoided, and thus the number of required input models is smaller. Density-functional band-structure calculations within the generalized gradient approximation were used in the structural minimizations. The most stable structure was based on $Ca(BaF_4)_2$ and was in the orthorhombic space group *Pbca* with lattice constants $a=1337$, $b=928$, and $c=891$ pm. The electronic density of states reveals an insulator with a band gap of around 4 eV.

The most promising group of materials for high-density solid-state reversible hydrogen storage is complex hydrides.[1–3] Sodium alanate (NaAlH$_4$) was an early reversible hydride in this family[4] and is by far the one most studied and closest to real applications.[1] Many of the early problems with slow hydrogenation kinetics of NaAlH$_4$ are solved,[5,6] but the international goal of a gravimetric density of 6 wt. % hydrogen[7] may not be reached in this system. Also, NaAlH$_4$ dissociates via two separate phase transitions with different plateau pressures, which is not desirable from a practical point of view.

One alternative complex hydride that thus far has attracted limited attention is calcium alanate, Ca(AlH$_4$)$_2$. The hydrogen content is 7.9 wt. % hydrogen, which may be extracted in the following three proposed dehydrogenation steps:[15]

$$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + \tfrac{3}{2}H_2 \qquad (1)$$

$$CaAlH_5 \rightarrow CaH_2 + Al + \tfrac{3}{2}H_2 \qquad (2)$$

$$CaH_2 \rightarrow Ca + H_2. \qquad (3)$$

The decomposition temperatures for the reactions above are around 200 °C, 260–550 °C, and 600–700 °C.[15] The last temperature range is too high to be of interest for onboard hydrogen storage, and for this application only the first two steps, releasing 5.9 wt. % hydrogen, are at most available for reversible hydrogen storage. The temperatures above are for the pure material, and it may be expected that the addition of a catalyst is going to lower the decomposition temperature significantly, based on what is seen for other alanates (even though such additives may decrease the hydrogen capacity somewhat).[4,16] Calcium alanate has been synthesized by reactions in nonaqueous solvents[17] and mechanochemically in the solid state.[15] The crystal structure has not been determined, possibly because of rapidly rotating AlH$_4$ tetrahedra. It is also not known whether reversible gas-phase hydrogenation at modest conditions is possible. This makes a theoretical prediction of the crystal structure important; when this

is known, it is also possible to calculate the thermodynamical stability of the relevant phases as a function of temperature by calculating the phonon spectrum. A cluster study has investigated the structure of Ca(AlH$_4$)$_2$ molecules,[18] but the small size of the models (one formula unit) makes the relevance of that work to the crystal structure of the solid phase limited.

Prediction of crystal structures from first-principles calculations is nontrivial when nothing is known about the cell size or symmetry. One possibility is to use many input models based on known crystal structures of similar compounds, either by keeping the cell size and shape intact[19] or by allowing them to relax.[20] The latter method reduces the number of input models necessary to span a sufficiently large part of the crystal structure space to ensure that the correct structure is found; however, it is still necessary to have access to a number of input models. One way to reduce the necessary number of input models further is to use simulated annealing, where molecular dynamics is used to simulate heating and cooling of a structure, starting from a guess structure.[21] This also requires several input structures, however, because many local minima may exist. It is also usual to keep the unit cell size and shape fixed during this procedure, which makes it possible to end up in a phase that is stable at another pressure than the ambient. In this paper another way of reducing the number of required input models is presented in which the symmetry of the input models is deliberately broken before the structural relaxation, making it possible to move away from any local minimum represented by the input models. This is compared to what is obtained from similar relaxations, starting from the models with unchanged symmetry.

The calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP),[22,23] which is a density-functional band-structure program using plane-wave basis sets. The projector augmented wave (PAW) method was used to span out the electron density,[24] and the gradient-corrected exchange-correlation potential was PW91.[25] The criterion for self-consistency in the electronic structure determination was that two consecutive total energies differed by

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TABLE I. The model structures used as input for the structural optimizations. Z is the number of formula units in the unit cell, and the coordination number $C_{A\text{-}C}$ counts the number of C atoms closer to an A atom than 3 Å in the structure AB_2C_8. The coordination number $C_{B\text{-}C}$ is always 4. The models in space group $P1$ are based on the model above, but with the symmetry deliberately broken. The symmetry after relaxation is shown with two thresholds a for the symmetry recognition, the relaxed volume is given in angstroms cubed, and the formation enthalpy H_{Form} at 0 K relative to CaH_2 and the elements in their standard state (Eq. (4)) is given in kilojoules per mole per formula unit.

No.	Model	Ref.	Z	$C_{A\text{-}C}^{In}$	Input symmetry	Output symmetry $(a=10^{-3})$	$(a=0.3)$	$C_{\text{Ca}-\text{H}}^{Out}$	Volume (Å^3)	H_{Form} (kJ/mol)
1	$CuAl_2Cl_8$	8	2	4	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	6	197	43.07
2	$BaAl_2Cl_8$	9	2	8	$P12/a1$	$P2/c$	$P2/c$	8	155	−25.64
3					$P1$	$P1$	$P2/c$	8	158	−25.27
4	$CuAl_2Cl_8$	10	2	4	$P2_1/c$	$P2_1/c$	$P2_1/c$	8	138	2.68
5					$P1$	$P1$	$P2_1/c$	6	202	43.64
6	$MgAl_2Cl_8$	11	4	6	$I12/c1$	$C2/c$	$C2/c$	6	158	27.66
7					$P1$	$P1$	$C2/c$	6	196	29.48
8	CaB_2F_8	12	8	8	$Pbca$	$Pbca$	$Pbca$	8	144	−50.19
9					$P1$	$P\bar{1}$	$Pbca$	8	152	−49.76
10	$MgAl_2H_8$	13	1	6	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	6	164	−10.15
11					$P1$	$P\bar{1}$	$P\bar{3}m1$	6	175	−11.79
12	ZrW_2O_8	14	4	6	$P2_13$	$P2_13$	$P2_13$	6	182	−10.08
13					$P1$	$P1$	$P2_13$	6	182	−6.70

less than 0.01 meV. The cutoff energy was 780 eV, and the k-point spacing was always smaller than 0.03 Å^{-1} in reciprocal space. The tetrahedron method with Blöchl corrections was used to smear out the partial occupancy of the single-particle wave function. The calculated total energy was converged to within around 1 meV with respect to all the numerical errors mentioned above.

Since little has yet been reported on the crystal structure of $Ca(AlH_4)_2$, the search has been made as open as possible. It has previously been shown that input structures that are similar, that is with the same coordination numbers, often lead to degenerate structures.[20,26] The input models have therefore been chosen among compounds with the same stoichiometry found in the ICSD crystal-structure database[27] to give as large a variation in the coordination numbers as possible. Starting from each of these models, full geometrical optimizations have been carried out without any constraints on the atomic positions or cell parameters. Since band-structure calculations make use of symmetry operators to improve efficiency, however, some of the high-symmetry structures will never move away from their symmetry during relaxation. We have therefore created low-symmetry models by deliberately breaking symmetry (by changing cell parameters and ionic positions) down to triclinic $P1$ for all the models except one (which starts as triclinic $P\bar{1}$). Also, some of the models being tested were not possible to relax or led to unreasonable crystal structures—they are not presented in this study. This led to the 13 input models listed in Table I. The relaxations were performed by using the residual minimization method with direct inversion in iterative subspace, an implementation of the quasi-Newton method. The ionic coordinates, unit cell size, and unit cell shape were optimized simultaneously. This eliminates structures with internal stress

and is a very efficient way of searching through a large part of the relevant crystal-structure space.[26] The structure was considered relaxed when all forces were less than 0.05 eV/Å. A single calculation using high accuracy was performed after the completed relaxation to determine the accurate total free energy. The FINDSYM program from the ISOTROPY package[28] was used to determine the symmetry of the various structures.

The resulting crystal structures and total energies for the various input structures are shown in Table I. We first note that, if relatively strict symmetry recognition is used (the accuracy parameter $a=10^{-3}$), all the original models (without broken symmetry) remain in their initial space group, while the $P1$ models either end as $P1$ or $P\bar{1}$. However, since the relaxation procedure is stopped before true equilibrium, it is more relevant to look at the symmetries resulting from a higher threshold symmetry recognition ($a=0.3$). We then see that all the $P1$ models have at least retained the symmetry from which they were moved, and that No. 1 has increased symmetry from $P\bar{1}$ to $P2_1/c$. Was it then unnecessary to include the models with broken symmetry? A closer inspection of the output structures shows that most of these models indeed end up with the same structure as the original without broken symmetry, but with one exception. Model No. 5 has the same space group as No. 4, but $C_{\text{Ca}-\text{H}}$ and the volume are different. It turns out that No. 5 has moved to the same structure as No. 1, a structure with larger volume and lower coordination number than No. 4. This illustrates how it is possible to occasionally move out of a local structural minimum by breaking the symmetry of a high-symmetry phase. It also shows that, if the selection of input models is large and representative, this other local (or global) minimum may correspond to another structure model that is already repre-

sented. This opens two choices for an efficient search of unknown crystal structures: Either we should use as many input models as possible, keeping the original symmetry, or we should include models with their symmetry deliberately broken in a smaller set of input models. Which method to use depends on several factors, such as the number of nonequivalent input models available, the unit cell size of alternative input models, and how efficiently the software handles low-symmetry structures relative to high-symmetry ones.

Models 4 and 5 also illustrate another aspect: It is possible to change coordination numbers during quasi-Newton relaxation. The input models had $C_{Ca—H}=4$, and this increased to 6 and 8 for models 5 and 4. It also emphasizes the importance of variation of the coordination numbers. Even though the coordination numbers of models 4 and 5 ended similar to all the others, the final structures were not equivalent, so that another part of the crystal structure space was investigated by these models. All the models that gave reasonable output structures ended with $C_{Ca—H}=6$ or 8. As mentioned above, some input models gave unreasonable structures, with large voids and unbonded atoms. Other models were impossible to relax, even when trying repeated times with different relaxation schemes. All these models had coordination numbers different from those in Table I, either $C_{Ca—H}$ or $C_{Al—H}$ (the latter was 4 for all reasonable structures). From this we may quite safely conclude that the real structure of Ca(AlH$_4$)$_2$ has $C_{Al—H}=4$ and $C_{Ca—H}=6$ or 8. There is a clear connection between volume and coordination numbers: $C_{Ca—H}=8$ if the volume is less than 158 Å^3, and 6 if it is larger.

We now turn to the thermodynamic stability of the models. The formation enthalpy of Ca(AlH$_4$)$_2$ at 0 K was calculated according to the tentative formation from CaH$_2$

$$\Delta H_{Form}[Ca(AlH_4)_2] = E[Ca(AlH_4)_2] - E(CaH_2) - E(Al) - 3E(H_2), \quad (4)$$

where $E[Ca(AlH_4)_2]$ is the uncorrected total free energy of Ca(AlH$_4$)$_2$ as calculated by VASP, etc. CaH$_2$ and the elements are calculated in their standard state. The most stable structure in Table I is No. 8—the *Pbca* structure based on CaB$_2$F$_8$. It is around 25 kJ/mol more stable than the second most stable structure and is, thus, our best suggestion for a crystal structure for Ca(AlH$_4$)$_2$. The formation enthalpy is around −50 kJ/mol=−12.5 kJ/mol H$_2$, which is stable compared to CaH$_2$ and the elements. This is quite similar to NaAlH$_4$, where the formation enthalpy related to the first decomposition reaction has been calculated to be −10.5 kJ/mol H$_2$,[29] so it gives hope that the hydrogenation of Ca(AlH$_4$)$_2$ may be reversible at reasonable conditions, provided the kinetic barriers are not too high.

The relaxed *Pbca* structure of Ca(AlH$_4$)$_2$ is presented in Table II and in Fig. 1. Hydrogen is coordinated around Al in slightly distorted tetrahedra—the Al—H distances vary from 161 to 163 pm, while the H—Al—H angles vary from 106.8° to 113.2°. Ca is eight coordinated to H in distorted square antiprisms, with each corner shared by an AlH$_4$ tetrahedron. The structure is relatively loose with quite large voids. This may help to explain why it has been difficult to resolve the structure experimentally, since it is probable that

TABLE II. The proposed structure for Ca(AlH$_4$)$_2$. The space group is *Pbca* (No. 61), and the lattice constants are $a=1337$, $b=928$, and $c=891$ pm. All the atoms are in Wyckoff position c(8), and the number of formula units in the unit cell Z=8. The uncertainty of the atomic coordinates is in the order of 0.01 due to the relaxation procedure.

Atom	x	y	z
Ca	0.11	−0.47	0.22
Al$_1$	−0.06	−0.22	−0.01
Al$_2$	0.16	−0.11	0.32
H$_1$	−0.01	−0.34	0.11
H$_2$	0.13	0.39	0.41
H$_3$	0.13	0.31	0.12
H$_4$	0.02	−0.37	0.41
H$_5$	0.17	−0.08	0.50
H$_6$	0.04	−0.09	0.27
H$_7$	0.19	−0.27	0.27
H$_8$	0.22	0.01	0.23

the barrier of rotation for the tetrahedra is quite low. The number of decimals for the atomic coordinates is only two in Table II; this is because of the uncertainty arising from the relaxation procedure. The structures resulting from the models with original and broken symmetry differ by up to 0.01 in the coordinates, since the relaxation procedure must be stopped while the forces are nonzero, and a much stricter force-relaxation criterion is needed to increase the accuracy
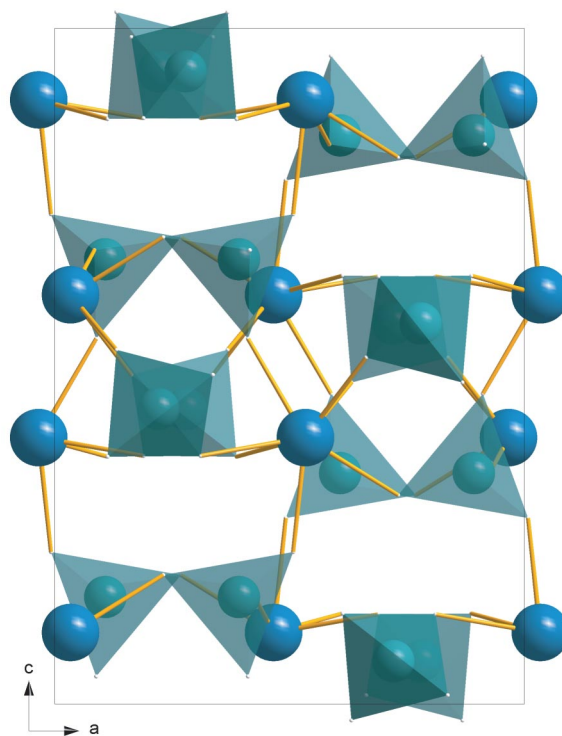

FIG. 1. (Color online) The proposed crystal structure of Ca(AlH$_4$)$_2$. The balls and tetrahedra represent the Ca atoms and AlH$_4$ complexes, respectively.
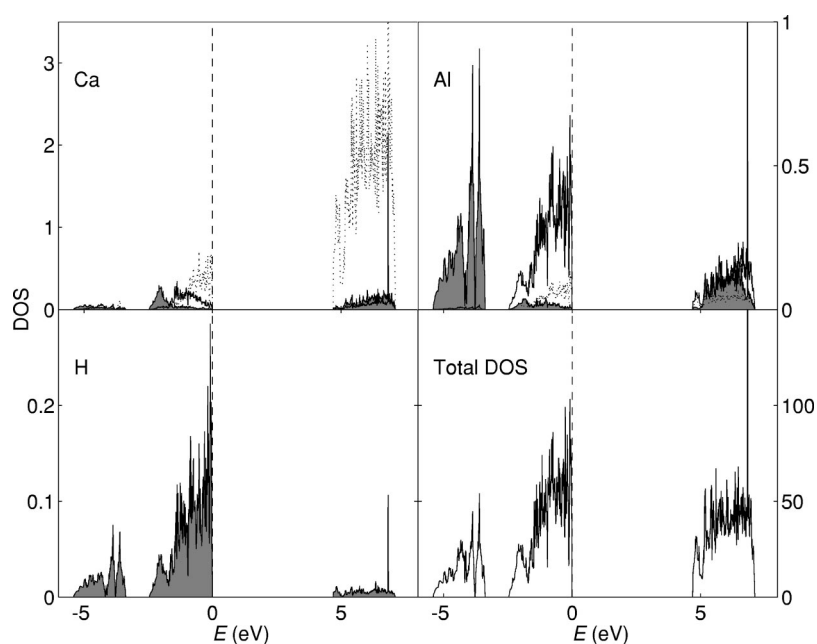
FIG. 2. Total and projected electronic density of states (DOS) as a function of the energy relative to the Fermi level. The most stable crystal structure (No. 8) was used in the calculation. The units are number of states per atom times energy for the projected DOS and number of states per unit cell for the total DOS. s-, p-, and d-projected DOS are shown as shaded-gray, solid, and dotted curves. Note the different scales for the different atoms.

of the atomic coordinates. This means that the determination of the space group is not 100% conclusive, but based on the direction of movement of the ions during the relaxation, it is highly probable that further relaxation with higher precision would lead to the same space group.

It is further possible that the inclusion of zero-point energy and temperature effects may lead to another crystal structure than the one presented above being most stable at room temperature. To clarify the extent of these effects, it would be necessary to calculate the phonon spectrum of the competing phases, but this is beyond the scope of this work. We do see, however, that the models that are closest to No. 8 in stability (Nos. 9, 2, and 3) have smaller volumes than where the change in coordination numbers take place. This means that even if the room-temperature structure is different from No. 8, it quite certainly has $C_{Ca—H}=8$ and $C_{Al—H}=4$. We may also relatively safely conclude that the unit cell volume is around 144 Å^3, which corresponds to a density of 1173 kg/m^3.

The calculated local and total density of states (DOS) based on the most stable crystal structure are shown in Fig. 2. From this figure we see that $Ca(AlH_4)_2$ is an insulator with a band gap of more than 4 eV. There are two main valence bands and one conduction band in the DOS. The lowest valence band is dominated by Al $3s$ electrons, with a small contribution from H $1s$ electrons and almost nothing from Ca. The upper valence band is divided into three parts. They are all occupied by Al $3s$ electrons and H $1s$ electrons, and in addition, the three parts are dominated by Ca $4s$, $3p$, and $3d$ electrons, respectively. The conduction band is primarily dominated by Ca $3d$ electrons and to lesser extent Al spd hybridized electrons. The overall features of the DOS are quite similar to those of $NaAlH_4$ and $Mg(AlH_4)_2$.[30,31] One

main difference is that the Na s and p states are energetically degenerate in Na alanate, while the s, p, and d states of Mg and Ca are well separated in Mg and Ca alanate. Another difference is that the conduction band of Al is both broader and higher in Na and Mg alanate than in Ca alanate. Whether any of these features has relevance to the hydrogenation properties of the alanates is still an open question.

In conclusion, a scheme of using first-principles calculations to determine crystal structures has been used to predict the crystal structure of $Ca(AlH_4)_2$. Six different structure models based on similar compounds were used as starting points for structural relaxation, with their symmetries explicitly broken down to $P1$. Similar relaxations were performed using the high-symmetry structures as input, and the same structure resulted in five of the cases. In the sixth case, the broken-symmetry model moved to a different structure, which was similar to the structure resulting from a seventh input model without its symmetry broken. The conclusion is that broken-symmetry models may help to find structures not included in the input structure set; alternatively, a large and representative set must be used in order to span out the largest possible part of the crystal-structure space.

The crystal structure of $Ca(AlH_4)_2$ has four-coordinated H in tetrahedra around Al, and H is eight coordinated around Ca. The most probable space group at low temperatures is $Pbca$, and the calculated density is 1173 kg/m^3. The electronic density of states shows that $Ca(AlH_4)_2$ is an insulator with a band gap of around 4 eV.

[1] A. Züttel, Mater. Today Sept., 24 (2003).

[2] G. Sandrock and R. C. Bowman Jr., J. Alloys Compd. **356–357**, 794 (2003).

[3] P. P. E. W. Grochala, Chem. Rev. (Washington, D.C.) **104**, 1283 (2004).

[4] B. Bogdanovic and M. Schwickardi, J. Alloys Compd. **253**, 1 (1997).

[5] B. Bogdanovic, M. Felderhoff, S. Kaskel, A. Pommerin, K. Schlichte, and F. Schüth, Adv. Mater. (Weinheim, Ger.) **15**, 1012 (2003).

[6] M. Fichtner, O. Fuhr, O. Kircher, and J. Rothe, Nanotechnology **14**, 778 (2003).

[7] *International energy agency hydrogen program, task 17*, http://www.ieahia.org/tasks/task17.html

[8] N. Kitajima, H. Shimanouchi, Y. Ono, and Y. Sasada, Bull. Chem. Soc. Jpn. **55**, 2064 (1982).

[9] P. Stegmueller, Ph.D. thesis, Universitaet Karlsruhe (1997).

[10] H. Schaefer, M. Binnewies, R. Laumanns, and H. Waechter, Z. Anorg. Allg. Chem. **461**, 31 (1980).

[11] M. A. Einarsrud, H. Justnes, E. Rytter, and H. A. Oye, Polyhedron **6**, 975 (1987).

[12] T. H. Jordan, B. Dickens, L. W. Schroeder, and W. E. Brown, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **31**, 669 (1975).

[13] M. Fichtner, J. Engel, O. Fuhr, A. Gloss, O. Rubner, and R. Ahlrichs, Inorg. Chem. **42**, 7060 (2003).

[14] M. Auray, M. Quarton, and M. le Blanc, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **51**, 2210 (1995).

[15] N. N. Mal'tseva, A. I. Golovanova, T. N. Dymova, and D. P. Aleksandrov, Russ. J. Inorg. Chem. **46**, 1793 (2001).

[16] D. Blanchard, H. W. Brinks, B. C. Hauback, and P. Norby, Mater. Sci. Eng., B **108**, 54 (2004).

[17] V. V. Gavrilenko, L. I. Zakharki, and Y. N. Karaksin, Zh. Obshch. Khim. **42**, 1564 (1972).

[18] A. S. Zyubin and O. P. Charkin, Zh. Strukt. Khim. **31**, 3 (1990).

[19] P. Vajeeston, P. Ravindran, A. Kjekshus, and H. Fjellvåg, J. Alloys Compd. **363**, L7 (2004).

[20] O. M. Løvvik and O. Swang, Europhys. Lett. **607**, 607 (2004).

[21] S.-C. Chung and H. Morioka, J. Alloys Compd. **372**, 92 (2004).

[22] G. Kresse and J. Hafner, Phys. Rev. B **47**, R558 (1993).

[23] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996).

[24] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[25] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992).

[26] O. M. Løvvik, S. M. Opalka, H. W. Brinks, and B. C. Hauback, Phys. Rev. B **69**, 134117 (2004).

[27] *The Inorganic Crystal Structure Database (ICSD)*, http://icsdweb.fiz-karlsruhe.de

[28] H. T. Stokes and D. M. Hatch, *ISOTROPY*, http://stokes.byu.edu/isotropy.html (2002).

[29] S. M. Opalka and D. L. Anton, J. Alloys Compd. **356–357**, 486 (2003).

[30] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvaag, and A. Kjekshus, Appl. Phys. Lett. **82**, 2257 (2003).

[31] O. M. Løvvik and P. N. Molin, Phys. Rev. B (to be published 2004).