Local-density-approximation study of LaS and SmS

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(Received 19 October 1987; revised manuscript received 21 January 1988)

Structural properties of LaS and SmS have been calculated within the local-density approximation (LDA) with use of a highly accurate general-potential linearized augmented-plane-wave method. The calculated lattice parameter of SmS is 7.6% smaller than the experimental value and, moreover, the calculations do not show any indication of the experimentally observed isostructural phase transition. Parallel calculations in which f-electron hybridization was suppressed yielded a lattice parameter and bulk modulus in good agreement with the observed values. Based on this and the good agreement obtained with experiment for the chemically similar compound LaS, we conclude that the LDA does not adequately describe the localization of the f electrons in SmS and that this failure of the LDA precludes its use in an adequate description of the structural properties of this material.

I. INTRODUCTION

As a result of its computational tractability, the local-density approximation (LDA) has made feasible accurate *ab initio* calculations of the structural and dynamical properties of a wide variety of real materials. In spite of the large number of applications in which LDA-based methods have proved reliable, there are indications that this approximation may not be adequate in some f-electron systems. In particular, recent total-energy calculations by Min *et al.*[1] do not find any indication of the experimentally observed γ-α isostructural phase transition in Ce. This transition is believed to be a localization-delocalization transition of the f electrons. In addition, in Ce as well as in Eu and Yb (Ref. 2) accurate LDA-based techniques have yielded equilibrium lattice constants considerably smaller than those observed. Calculations in which f-electron hybridization is suppressed yield values in better agreement with experiment implicating these states in the failure of the LDA.

Mixed-valence SmS exhibits a strongly first-order isostructural phase transition[3] at modest pressure (6.5 kbar) which is believed to result from the delocalization and hence participation in bonding of the f electrons under pressure. Thus this system may be a good one for characterizing the above-mentioned failure of the LDA. While there have been some self-consistent band-structure calculations[4–6] for SmS as far as we are aware there has been no detailed study of the applicability of the LDA to this material. Here we report LDA-based calculations of the total energy of SmS as a function of the lattice parameter using a highly accurate general-potential LAPW method. Parallel calculations were carried out with the Sm f electrons treated in an atomiclike approximation, thus suppressing their participation in the bonding in order to study the role these states play in the observed failure of the LDA.

II. RESULTS AND DISCUSSION

A. Structural properties

The calculations reported here were carried out with use of a general-potential linearized augmented-plane-wave (LAPW) method which has been discussed in detail elsewhere.[7] In this method both the potential and charge density are treated without shape approximations and both the valence and core electrons are treated relativistically (including spin-orbit effects), the valence electrons variationally, and the core electrons in an atomiclike approximation. In our calculation we used the Hedin-Lundqvist[8] exchange-correlation potential. Because the 5p core states are quite extended in the rare-earth metals, it was necessary to treat these as valence states in a separate energy window. Thus two energy windows were used, one for the valence electrons of Sm (La) and S and the other for the extended Sm (La) 5p core states. In order to establish the accuracy of our method in the absence of f electrons, a parallel calculation for the chemically similar compound LaS, which like SmS has a NaCl structure, was carried out. In Fig. 1 we show the calculated total energy versus volume for LaS, the solid line being a fit to the Murnaghan equation of state.[9] It is found that the calculated equilibrium lattice constant of 5.812 Å is within 1% of the experimental value[10] of 5.860 Å, the bulk modulus being 0.978 mbar. As far as we are aware there have been no experimental measurements of the bulk modulus of LaS. The calculation revealed that the choice of the La $l=1$ linearization energy parameter in the valence window is rather important. We placed it around S 3s energy level. Placing this energy parameter near the Fermi level yielded a contracted equilibrium lattice constant (by more than 4%). This is because in this material the sulfur 3s state is fairly extended and has a significant p-like weight when expanded about the lanthanum site. Choosing an energy parameter near the Fermi energy expels this charge from the lanthanum spheres, yielding an increase in the ionicity and therefore a contraction in the lattice parameter.

The calculations for SmS were carried out as much as possible parallel to those for LaS. The muffin-tin radii used were 3.00 a.u. for La, 2.50 a.u. for Sm, and 2.20 a.u. for S. We treated the Sm 5p states as band states in a second energy window. We placed the $l=1$ linearization energy parameter E_l in the valence window around S 3s energy level as was done for LaS. Sixty special **k** points[11] were used in performing the Brillouin-zone summations,

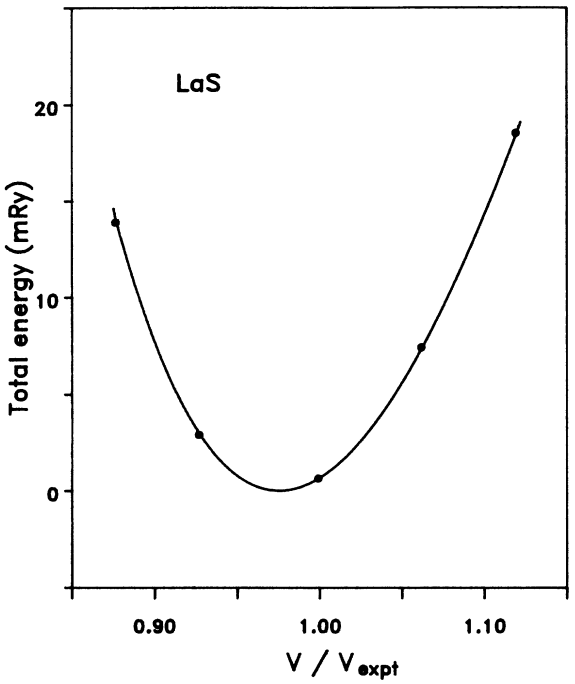

FIG. 1. Calculated total energy + 17 778.435 50 Ry vs volume for LaS. The solid line is a fit to the Murnaghan equation of state.

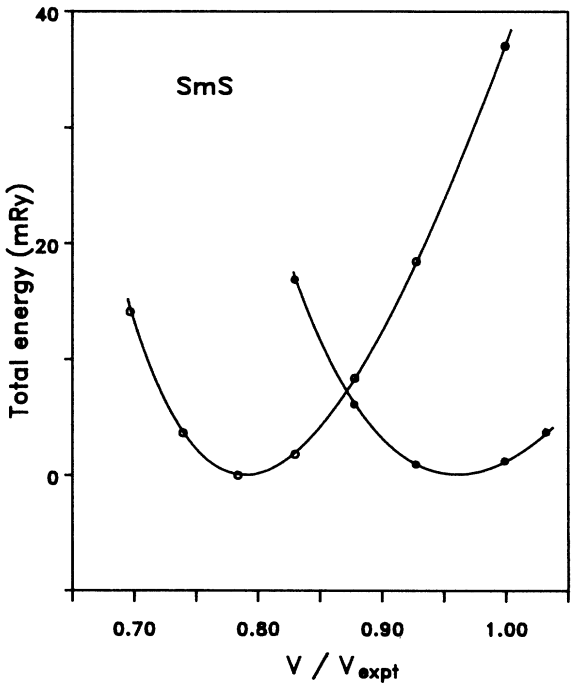

FIG. 2. Calculated total energy $-E_{\min}$ vs volume for SmS; open circles are for f electrons treated as valence electrons $E_{\min} = -21\,650.711\,03$, while solid circles are for f electrons treated as core electrons, $E_{\min} = -21\,650.568\,72$ (see text). The solid lines are fits to the Murnaghan equation of state.

yielding a total-energy convergence of the order of 10^{-4} Ry with respect to the number of **k** points. For LaS we used a basis set corresponding to $RK_{\max} = 8.6$, where R is the S muffin-tin radius and $K_{\max}$ is the plane-wave cutoff. For the volume range studied this cutoff yields between 280 and 380 basis functions. For SmS 290 to 700 LAPW basis functions were used, corresponding to $RK_{\max} = 9.0$. Calculations were performed using other basis-set cutoffs in order to check the convergence of the calculations, and it was found that the total energies were converged to within 1 mRy. Self-consistency was considered to be achieved when the total energy was stable to 10^{-5} Ry.

The total energy of SmS as a function of volume is shown in Fig. 2 and tabulated in Table I. It may be noted that the calculated total energy of SmS is a smooth function of the volume with no evidence of two energy minima or even of an anomalous softening. Thus, there is no indication of the experimentally observed semiconductor to metal (black to gold) isostructural phase transition, which takes place at 6.5 kbar,[3] or at about 90% of the equilibrium volume, even though we have performed calculations at expanded volumes for which the d-f hybridization vanishes. The failure to predict this phase transition in SmS using LDA was also noted by Strange,[4] though his calculation was not sufficiently self-consistent to yield reliable total energies. It is also consistent with the failure of LDA-based calculations for Ce,[1] where no evidence of the experimentally observed α-γ phase transition was found.

The calculated total-energy minimum in Fig. 2 occurs at a volume about 20% smaller than the experimental equilibrium volume. As shown in Table II, the Murnaghan equation-of-state fit which was performed excluding the two points at highly expanded volumes yields an equilibrium lattice constant 7.6% smaller than the experimental value and a bulk modulus over 50% larger than the experimental value[12] of 0.503 mbar.

Norman and Koelling[13] have reviewed the band-structure calculations for mixed-valence systems. They point out that LDA-based total-energy calculations predict contracted lattice constants, indicating that the LDA overestimates f bonding. The LDA substantially overestimates the bulk modulus for α-Ce (Refs. 1 and 14) and TmSe,[15] but is in accord with experiment for UPt_3.[16] The present calculation demonstrates that the LDA significantly underestimates the lattice parameter and

TABLE I. Calculated total energies +21 650 Ry vs lattice parameter for SmS ($a_{\text{expt}} = 11.289$ a.u.).

a (a.u.)	$E(a)$ (Ry)	a (a.u.)	$E(a)$ (Ry)
f as valence		f as core	
10.000	−0.696 88	10.600	−0.551 91
10.200	−0.707 33	10.800	−0.562 60
10.400	−0.711 00	11.000	−0.567 80
10.600	−0.709 18	11.276	−0.567 51
10.800	−0.702 60	11.400	−0.565 02
11.000	−0.692 53		
11.276	−0.673 93		
12.400	−0.567 54		
13.400	−0.463 45		

TABLE II. Equilibrium properties of SmS.

	SmS f as valence	SmS f as core	Expt.
Lattice constant (Å)	5.515	5.887	5.974
Bulk modulus (kbar)	843	608	503
dB/dP	4.9	4.2	2.4

overestimates the bulk modulus for SmS.

As mentioned, it is thought that the underestimation of the equilibrium lattice constants in these systems is due to the LDA overestimating the extent of $4f$ bonding. Even though the calculated lattice parameter is closer to that expected for the metallic phase (extrapolating the equation of state for metallic SmS of Ref. 3 to zero pressure yields an equilibrium volume about 11% smaller than that of the semiconducting state as compared to the LDA result of -20%), the LDA cannot be said to be describing this mixed-valence state correctly. This is because a correct description of the mixed-valence phase requires a correct description of the highly correlated f electrons which the LDA fails to provide. This is reflected in the relatively poor equilibrium lattice parameter. It has been shown in Ce,[1] Eu, and Yb (Ref. 2) that when the $4f$ electrons are treated as core electrons, the calculated equilibrium lattice constants (otherwise severely underestimated) are quite close to experiment. In order to determine whether this is also the case in SmS, we performed a total-energy calculation with the $4f$ electrons treated as core electrons, i.e., we suppressed the $4f$ hybridization. The resulting total energies are listed in Table I and displayed in Fig. 2. This calculation yields an equilibrium lattice constant of 5.89 Å which is much closer to the experimental value of 5.97 Å. The calculated bulk modulus $B = 608$ kbar is only about 20% larger than experiment.

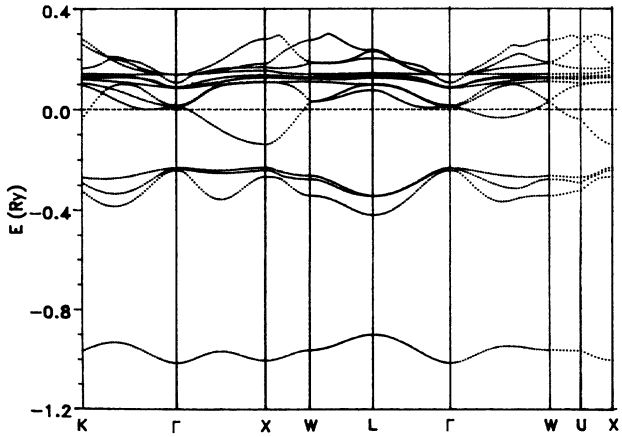

FIG. 3. Band structure of LaS at the experimental volume; dashed line indicates the Fermi level.

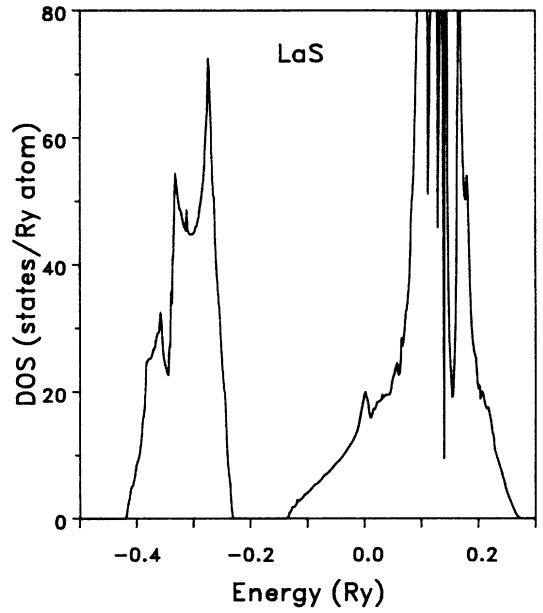

FIG. 4. Density of states of LaS at the experimental volume.

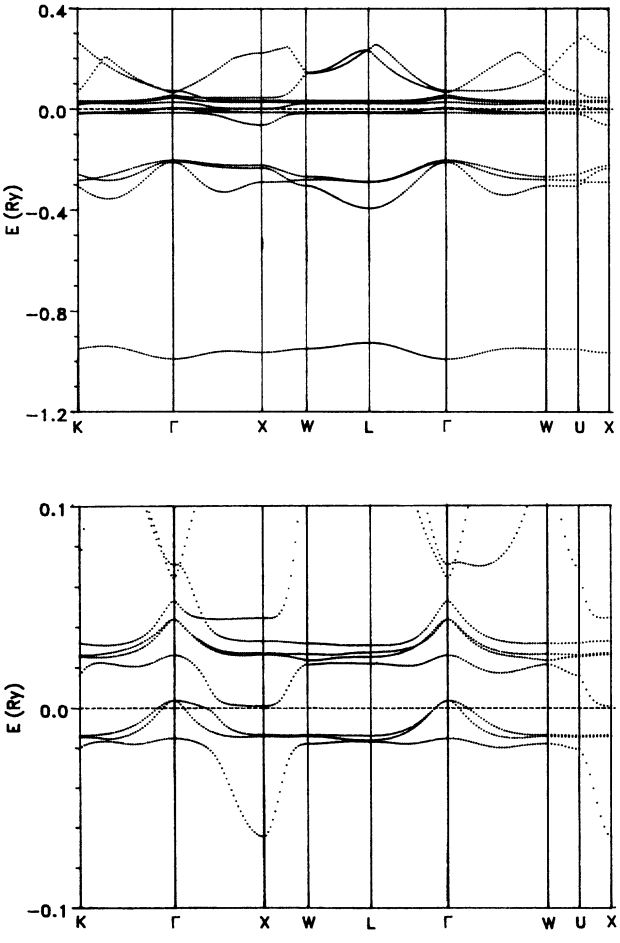

FIG. 5. Upper panel: Band structure of SmS at the experimental volume. Lower panel: A detailed view of the band structure about the Fermi energy.

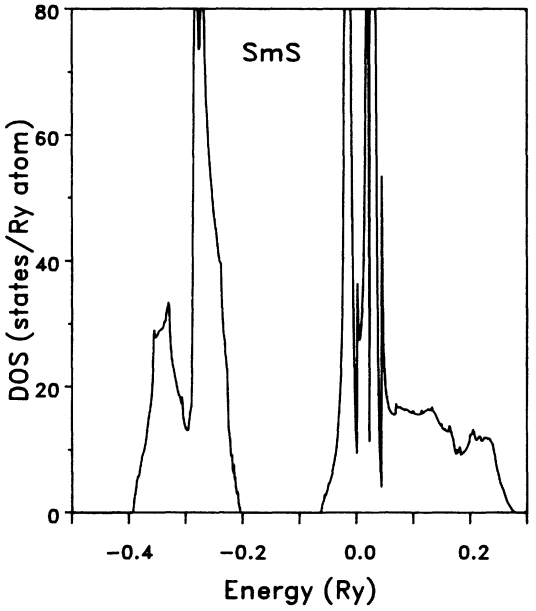

FIG. 6. Density of states of SmS at the experimental volume.

B. Band structure

Our calculated relativistic band structure for LaS at the experimental lattice parameter is shown in Fig. 3. The corresponding density of states (DOS) shown in Fig. 4 is similar to that obtained by Vlasov and Farberovich[17] using an independent self-consistent LAPW method. There is a low-lying S $3s$ band about 1 Ry below the Fermi energy E_F, a higher S $3p$ band about 0.3 Ry below E_F, and a partially occupied La $5d$ band near E_F. The unoccupied La $4f$ bands lie above E_F. The calculated band structure and corresponding DOS for SmS at the experimental lattice parameter are shown in Figs. 5 and 6, respectively. An expanded view of the DOS near E_F is shown in Fig. 7. The S $3s$ and S $3p$ bands are similar to those in LaS, but the $4f$ bands of Sm are now partially occupied. The band structure and DOS at a compressed lattice parameter of 10.4 a.u. (which is near the calculated energy minimum of Fig. 2) is shown in Figs. 8 and 9. Comparing Figs. 5 and 8, it is seen that as the volume is reduced the d and f bands become increasingly hybridized, and the f bands become broader. Scalar-relativistic calculations indicate that the spin-orbit interaction can alter the f-band positions by as much as 20 mRy. As mentioned, our total-energy results implicate the d-f hybridization in the isostructural phase transition, since we have shown that suppressing this hybridization yields an equilibrium lattice parameter near that of the semiconducting phase. The LDA results tend to overestimate the amount of hybridization, resulting in a contracted lattice parameter and no localization-

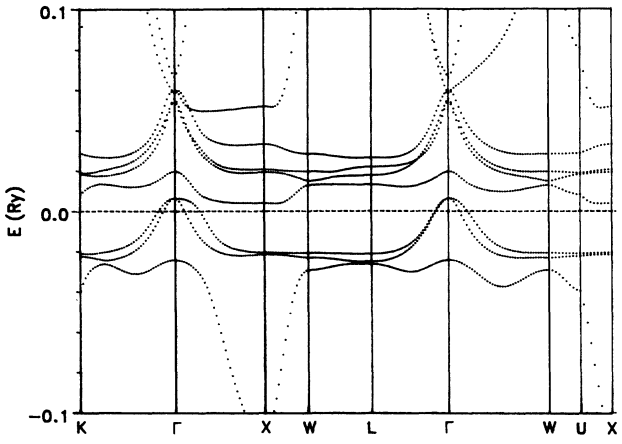

FIG. 8. Detailed view of the band structure of SmS at $a = 10.40$ a.u.

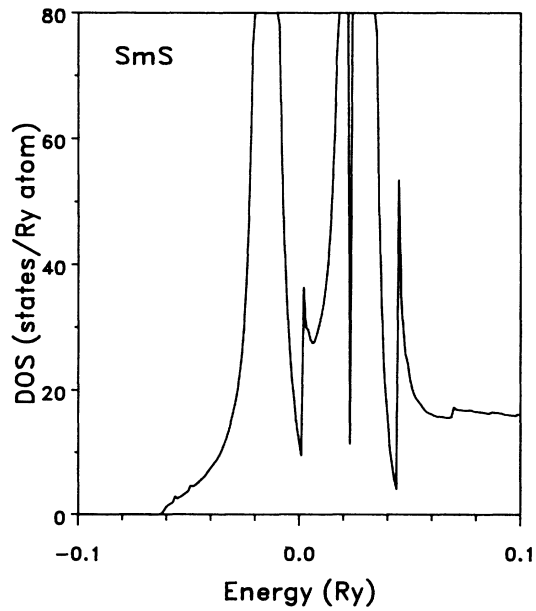

FIG. 7. Detailed view of Fig. 6 about the Fermi energy.

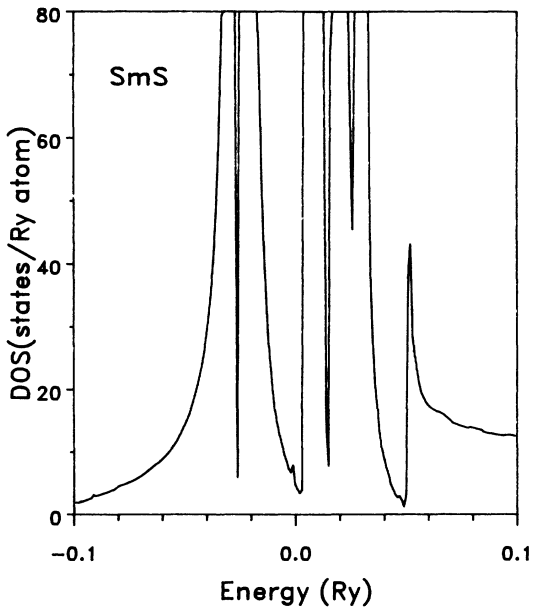

FIG. 9. Detailed view of DOS about the Fermi energy at $a = 10.40$ a.u.

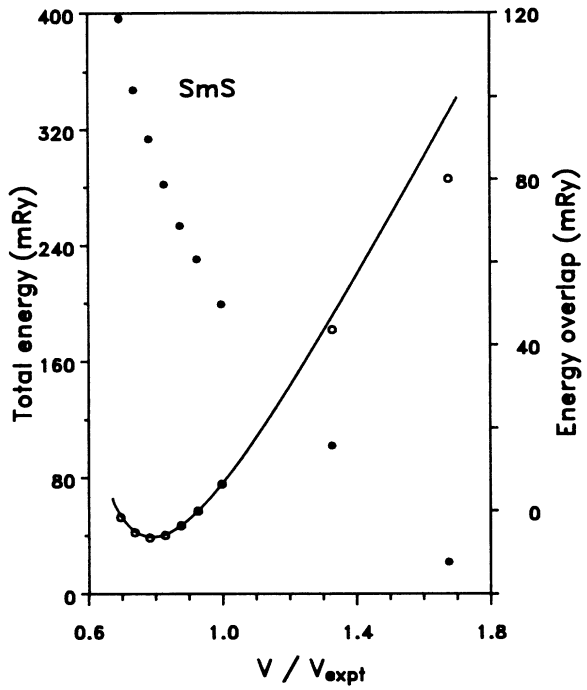

FIG. 10. Variation of d-f overlap with volume as defined in the text. The total energy softens at larger volume, but there are no indications of phase transition. The solid curve is the fit to the Murnaghan equation of state around the equilibrium volume and its extrapolation to large volume. The solid circles are for the overlap, the open circles are for the calculated total energy +21 650.750 00 Ry.

delocalization transition. In view of this failure to correctly describe the f electrons in SmS, the bands in Figs. 5 and 8 cannot be expected to provide reliable quasiparticle energies or dispersions.

It may be noted from Figs. 5 and 8 that there is a considerable amount of d-f hybridization even at the equilibrium volume. In order to investigate whether the LDA incorrectly predicates a phase transition when this hybridization diminishes at very large volumes we performed total-energy calculations at two highly expanded volumes. We take the energy difference between the flat occupied f band and the bottom of the d band at the X point as an indication of the amount of f-d overlap. This "overlap" is plotted along with the total energies at large volumes and the Murnaghan equation-of-state fit (see Fig. 2) in Fig. 10. At the largest volume studied this overlap vanishes, but there is still no indication of a phase transition.

III. CONCLUSIONS

We have reported total-energy calculations on LaS and SmS using an LDA-based LAPW method. We found that the LDA successfully predicts the equilibrium lattice constant of the non-f-electron system LaS. For SmS, the LDA underestimates the lattice parameter by 7.6%. Furthermore, we find no evidence for the experimentally observed isostructural phase transition in the calculated total-energy curve. When calculations are carried out treating the localized $4f$ electrons as core electrons, thus suppressing the hybridization of $4f$ electrons, the equilibrium lattice constant is much closer to experiment and the otherwise severely overestimated bulk modulus is within 20% of the experimental value. This confirms that LDA overestimates the f-electron hybridization in this material.

Thus, we conclude that the LDA provides an inadequate description of the f electrons in SmS.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation through Grant No. DMR-84-16046. Computations were carried out under the auspices of the National Science Foundation at the National Center for Supercomputing Applications (NCSA) at the University of Illinois at Urbana-Champaign.

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