Contents

1 Introduction **1**

1.1 Transition Metal Nanoalloy clusters 2

1.2 Transition Metal Nano-oxide clusters 2

1.3 Disordered Alloys 2

2 Objective **4**

3 Organisation of thesis **6**

4 Chapters **7**

5 Results **10**

6 Conclusion **14**

7 Achievements **16**

Bibliography **17**

Chapter 1

Introduction

A study of binary systems in cluster (confined system) as well as in bulk is of great technological relevance and is also physically intuitive. The basic types of structures that can be formed for mono-atomic clusters are now well-established. For example Lennard-Jones clusters[1] provide a well-characterized archetypal model for systems with isotropic interactions. However, the situation for *binary clusters* is potentially more challenging, and the new types of structures that can be stabilized by the presence of two different atom types are only beginning to be mapped out.

Considering the scenario in bulk, the discovery of binary alloys like brass (formed by alloying copper and zinc), bronze (formed by combining copper with a small proportion of tin) and steel (formed by alloying iron with a small amount of carbon) has remarkably improved the quality of human life. Alloying two or more constituents is one of the most successful processes in the search for new materials. Therefore, the study of the electronic structure of alloys is an important area of research in materials physics. By definition, alloys are multi-component systems which primarily exhibit metallic bonding and may contain one or more phases. In the present study we will be studying the effect of randomness in *binary alloys*.

1.1 Transition Metal Nanoalloy clusters

In recent times nanoalloy clusters have received considerable attention for their peculiar catalytic, optical, magnetic, electronic, and geometric properties[2, 3, 4, 5, 6]. For such clusters, chemical and physical properties can be tailored by varying not only the size but also the composition for a specific purpose. This opens the way to a large variety of potential applications in areas such as high-density recording[7], catalysis[8, 9, 10], optics[11, 12, 13] and biomedical studies[14]. So the first study that we made (Chapter 3 of the thesis) is on a transition metal nanoalloy cluster system.

1.2 Transition Metal Nano-oxide clusters

Extensive studies have been performed to characterize transition metal clusters and recently interest has expanded to transition metal oxides due to applications as model systems in heterogeneous catalysis and materials science on a microscopic level[15, 16]. By some estimates 90% of all commercially produced chemical products involves catalysts at some stage in the process of their manufacture. Catalysis is the acceleration of a chemical reaction by means of a substance, called a catalyst, which is itself not consumed by the overall reaction.

1.3 Disordered Alloys

The most common disordered alloys are substitutionally disordered alloys. These alloys have underlying lattice structure but each lattice point is occupied randomly by the constituent atoms. Thus the system lacks lattice translational symmetry. The difficulty arising due to this loss of periodicity is overcome by introducing mean-field theories[17, 18, 19, 20]. In these approaches, the disordered system is replaced by a lattice periodic effective medium, with effective atoms occupying lattice sites. One of the most successful mean-field approximations is the coherent potential approximation (CPA)[21]. However, whenever local environmental effects become important: like short-ranged ordering, chemical-affinity-driven local clustering, or if we

are dealing with rough surfaces and interfaces, the augmented space recursion(ASR)[22] is one of the more powerful techniques available. It goes beyond standard mean-field approximations to consider randomness not only at a site but also in its near neighbourhood. ASR also provides a formally exact way of dealing with off-diagonal disorder. This happens in alloys whose constituents have large differences in atomic radii leading to local lattice distortion effects whenever unlike-atoms surround one another. This is usually observed when alloying is done between atoms coming from different rows of the periodic table and are called non-isochoric.

Chapter 2

Objective

As far as study of transition metal nano-alloy clusters are concerned, the candidates chosen for this study, Mn and Co have very interesting properties in low dimensions. Manganese, though anti-ferromagnetic as bulk, shows finite magnetic moment in reduced dimension[24, 25, 26, 27] whereas, Cobalt shows enhanced magnetic moment compared to the bulk[28, 29, 30]. Therefore, it will be interesting to see how the properties of the bimetallic cluster formed out of these two elements change with composition, atomic ordering, and size.

Very few experimental studies on group VII transition metal (Re, Mn) oxide clusters exist in literature. But Manganese Oxide clusters are extremely important not only as catalysts and in the magnetic media but also in Mn-based single molecular magnets. It also takes essential part in a variety of biological processes from photosynthesis to bacterially mediated organic matter decomposition. Thus it becomes necessary to characterize MnO clusters thoroughly and systematically. This we attempt to do through our study of transition metal nano-oxides in our thesis.

In our study of disordered alloys, we first attempt to formulate a real space based methodology using the augmented space recursion (ASR) technique[22] to study the effect of subsitutional disorder on single-band and multi-band superconductivity in model binary alloy systems.

The major step towards constructing first principles tight-binding Hamiltonians began with the tight-binding, linearized muffin-tin-orbitals method (TB-LMTO)[31]. The TB-LMTO in

combination with ASR (TB-LMTO-ASR)[23] has proved to be extremely efficient to study electronic structure of substitutional disordered alloys. We extend the TB-LMTO-ASR in this thesis to deal with non-collinear magnetism to study the effect of disorder on non-collinear magnetism in binary alloys. We have applied our methodology to MnPt alloy system.

Chapter 3

Organisation of thesis

The thesis entitled "A Study of the Effect of Disorder and Confinement on Binary Systems" begins with the "Certificate From the Supervisor". Then the Dedication, "Acknowledgments", "Publications", "Contents", "List of Figures" and "List of Tables" follow. The rest of the thesis is organised into chapters as discussed in the next Chapter of the abstract and then the bibliography for the entire thesis follows.

Chapter 4

Chapters

Chapter1 is the "Introduction" to the thesis where the importance of studying binary systems is discussed and the contents of the various chapters of the thesis are mentioned briefly.

Then in "Chapter 2" we present an overview of the Density Functional Theory which describes the ground state properties of a many electron system in terms of the density of the system. This theory forms the backbone of our study of the electronic structure of the MnCo and MnO clusters and MnPt alloy in our subsequent chapters.

In the next chapter, "Chapter 3", we systematically and thoroughly investigate the structural, electronic and magnetic properties of Mn-Co clusters within the *ab-initio* pseudo-potential plane wave method using generalized gradient approximation for the exchange correlation energy. In Co-rich clusters the magnetic moment is enhanced by Mn addition unlike in the bulk. Certain Mn rich clusters are found to be ferri-magnetic. The enhancement of magnetic moment of Mn-Co clusters when a Co atom is replaced by a Mn atom is found to be independent of the size and composition (as long as there is no change in the magnetic nature of the cluster on Mn inclusion). The interplay of bond lengths and coordination in determining the magnetic moment of clusters is also analyzed in this chapter.

In "Chapter 4" we observe an unusual evolution of structure and magnetism in stoichiometric MnO clusters based on an extensive and unbiased search through the potential-energy surface within the Density Functional Theory (which is discussed in details in an earlier chap-

ter). The smaller clusters, containing up to five MnO units, adopt two-dimensional structures; and regardless of the size of the cluster, magnetic coupling is found to be anti-ferromagnetic in contrast to previous theoretical findings. Predicted structure and magnetism are strikingly different from the magnetic core of Mn-based molecular magnets, whereas, they were previously argued to be similar. Both these features are explained through inherent electronic structures of the clusters.

In "Chapter 5" we have discussed the recursion technique introduced by Haydock as a very efficient method to calculate electronic structure properties of even those systems which lack lattice translational symmetry. Along with this we shall also introduce and discuss the Augmented Space Formalism which is a very useful technique for disorder averaging in random systems. These together form the Augmented Space Recursion technique, a method which we have used extensively to calculate various properties of model and real disordered systems in the subsequent chapters.

In "Chapter 6" we present a real-space approach to study the effect of disorder on superconductivity. Our method of disorder averaging is the augmented space formalism which was introduced in the previous chapter. We shall apply our method to two situations : first, a tight-binding, negative U Hubbard model with only on-site disorder and next a random negative U Hubbard model where electrons attract each other provided they are near certain randomly placed centers. Having established our method in these two well studied limits, we shall consider the physics of superconducting alloys with correlated disorder. Since the mean-field single-site approximation techniques cannot deal with short-ranged order, the advantage of the augmented space technique which goes beyond mean-field approximations for configuration averaging, will become immediately evident. We will also illustrate the viability of our methodology for systems with off-diagonal randomness. Off-diagonal randomness for example is realized in alloys where there is a local lattice distortion because of size mismatch of the constituents, and introduces disorder in the off-diagonal hopping integral in a tight-binding model.

In "Chapter 7" we will extend our methodology to study the effect of disorder on single band

superconducting systems to analyze the effect of disorder on multi-band systems. We again use the augmented space formalism to handle disorder. In the ordered regime our results for both intra-band and inter-band pairing are in excellent agreement with the existing results. Having verified the reliability of our method we use it to investigate the survival of superconductivity in the presence of disorder in multi-band systems.

In "Chapter 8" we have developed a formalism by combining the tight binding linearized muffin-tin orbital and the recursion methods with the augmented space formalism (TB-LMTO-ASR) to study non-collinear magnetism in disordered alloys. We apply the TB-LMTO-ASR to study disordered MnPt alloy. Electronic structure of this alloy in different magnetic structures have been calculated and compared to the previous theoretical results.

In the concluding chapter, "Chapter 9" we have discussed the developments made and objectives achieved in this thesis work and the scope for future developments that this work has opened up.

Chapter 5

Results

In our study of nano-alloy clusters we have studied structure, bonding, and magnetism in small bimetallic Mn_xCo_y ($x + y$=2-5) clusters from first-principles DFT calculation. Due to weaker bonding among Mn-atoms and relatively strong Co-Co bonding than Mn-Co bonding, the binding energies of the alloy clusters decrease with increasing Mn-concentration. Interesting effects in binding energy, stability and magnetism in the nanoalloy clusters are explained through the interplay between bond length and coordination. The Co-rich clusters are found to be ferromagnetic unlike the bulk alloy and the corresponding magnetic moment is higher than the pure Co_n clusters as is seen in the recent SG experiments.[32, 33] Moreover, the magnetic moment of Co-rich nano-alloy clusters increase with Mn-concentration and this increment is 2 μ_B/Mn-substitution and is independent of cluster size and composition. Co-atoms are found to be more magnetically polarized in a Co-rich environment than in Mn-rich one, i.e., likewise in bulk alloy, as the environment is made more Mn-rich, the average μ_{Co} decreases.

In our study of nano-oxide clusters we have demonstrated, through a rigorous and unbiased potential energy search, that the stoichiometric MnO nanoclusters show unusual 2D structures, and that Mn atoms are AFM coupled, and both the features are explained in terms of the inherent electronic structure of these nanoclusters. Present results deviate from the earlier theoretical predictions as the previous studies explored only a subspace of the potential energy surface limited by the high symmetry structure and ferromagnetic coupling[34, 35, 36, 37].

Although the experimental results on such clusters are scarce, the present results agree well with the limited experimental predictions on the cluster structure and stability[38].

In our study of the effect of disorder on single-band superconductivity in binary alloys we have proposed the augmented space vector recursion (ASVR) method as a very effective real space approach to study the effect of disorder on superconductivity beyond the mean-field approximation. We have established the accuracy of our method by comparing its results with those obtained by other techniques, for both s- and d-wave superconductors. We have seen that while for s-wave superconductors the gap in the quasi-particle spectrum survives even in the presence of disorder, (the system being in the limit of validity of Anderson's theorem), for the exotic d-wave case it vanishes in the presence of slightest disorder. In addition, considering a system where electrons attract each other provided they are near certain centers, we see a critical number of such centers are necessary for superconductivity to survive in the system. Our results using the ASVR method are in excellent agreement with that available in the literature.

Satisfied about the reliability of our method, we use it to study the effect of environment dependent randomness of various terms of the Hamiltonian. This would not have been possible using any single-site mean-field approximations like the CPA. For correlated disorder in ε_i segregation tendency support superconductivity while for a system where only some sites are interacting, ordering facilitates tunneling of Cooper pairs from interacting to non-interacting sites and thus favors superconductivity. However for higher value of the effective pair interaction potential U the coherence length falls off and such tunneling of Cooper pairs become difficult.

In this study we have also applied the augmented space vector recursion (ASVR) method to study the effect of randomness in the off-diagonal terms of the attractive Hubbard Hamiltonian on s- and d- wave superconductivity. For binary substitutional alloys we see that for s-wave superconductivity inclusion of correlated simultaneous configuration fluctuation at two sites ($\chi \neq 0$) has a strong influence on the superconducting gap which cannot be captured using methods involving single site approximation. It is in the ability to successfully deal with off-diagonal disorder that the strength of our technique (ASVR) is especially manifested. Further

in the presence of off-diagonal disorder s-wave superconductivity is favoured by greater hopping integral strength between same kind of species as compared to that between different kinds.

For d-wave superconductors randomness in t_{ij} causes gap-less superconductivity similar to the case when disorder is included in the diagonal terms. Combined diagonal and off-diagonal randomness causes asymmetry of DOS in both normal and superconducting binary substitutional alloys only when the band widths of the individual DOS of the A and B species are different.

In our study of multi-band superconductivity we have established the accuracy of our method by comparing our results with those obtained using other techniques in the ordered situation. We have seen two-gapped situation in the presence of intra-band pairing. In the presence of inter-band pairing although there is only a single kind of pairing thus a single pairing amplitude, two different gaps open up if the band structure of the bands are different. For this kind of pairing we have also obtained the non-superconducting, the breached and the BCS superconducting regimes by varying the inter-band pairing potential.

We have studied the effect of randomness in one channel on the other. When only intra-band pairing occurs, then randomness in one channel does not affect the other. But in the presence of inter-band pairing both the bands are affected by randomness in any one of the channels. Here too by varying the inter-band Hubbard parameter the three paradigms, namely, the non-superconducting, breached and BCS superconducting regimes may be obtained, but the threshold potential required to crossover from one regime to another is much higher.

By increasing the strength of disorder its seen that although superconductivity survives when intra-band pairing occurs, in the presence of inter-band pairing the gaps in both the channels close up with increasing disorder.

Our calculation indicates inter-band pairing which was not considered in earlier work is not only interesting but opens up a paradigm beyond Anderson's theorem to understand superconductivity in disordered systems.

In the chapter on study of non-collinear magnetism in binary disordered alloys, we have set up a computational framework for the study of non-collinear magnetic phases in disordered

alloys based on the marriage of three distinct techniques : the TB-LMTO, the recursion method and the augmented space formalism. We have used our formalism to study disordered MnPt alloy. The very small energy differences between different non-collinear phases means that our error window should be very narrow. The augmented space formalism is formally exact, therefore the error arises in the recursion method and the TB-LMTO. Errors in the former are controlled and can be estimated. It is in the TB-LMTO that is the main source of error. A way out is either to replace TB-LMTO with the more accurate TB-KKR. This would lead to energy dependent potential parameters and hence energy dependent recursion. This has been developed by us earlier[39]. Alternatively we can use the full-potential LMTO. But in that case, the Hamiltonian is not sparse and we have to have a re-look at the errors in the recursion method. This work is now in progress.

It appears that no detailed experimental investigation into non-collinear magnetism in disordered MnPt alloy has been carried out to confirm our predictions. Until this is carried out, we have only the theoretical analyses at hand.

Chapter 6

Conclusion

Both the transition metal nano-alloy and nano-oxide clusters studied show great potential for industrial usage. Mn atoms being half-filled have a large number of unpaired electrons (5) and thus large atomic moment. But in bulk since pure Mn or even MnCo alloys are antiferromagnetic thus the total moment gets quenched. However in MnCo alloy clusters we see as long as the clusters are Co-rich they remain ferromagnetic and thus their net moments are much enhanced from the corresponding pure Co clusters. $(MnO)_x$ clusters for x=2 to 8 are antiferromagnetic like bulk. But Mn_x clusters are ferromagnetic for x < 5. Thus there is a transition of magnetic state of Mn_x clusters for x=2 to 4 from ferromagnetic to antiferromagnetic upon oxidation. This ability to chemically tune the magnetism in Mn clusters can be of great technological relevance. Infact a structural transition of Mn_x clusters also occur (from 3 dimensional to 2 dimensional) for x=4 and 5 upon oxidation. In future we intend to trace out the path of this magnetic and structural transition by studying off-stoichiometric manganese-oxide clusters.

For MnCo clusters we find it is necessary to carry out calculations for not only the ground states but also the low energy isomers for comparison of theoretical results with Stern-Gerlach (SG) experiments since in the SG beam the isomers are also present with a statistical weight. This is because the experiments are all carried out at very low but finite temperatures. Although for Manganese-Oxide clusters experimental reports are rare, still it is essential to investigate the isomers of such clusters to be prepared to correspond theoretical results with future experiments.

The studies on model disordered binary alloys are in an attempt to understand the effect of disorder on single and multiband superconductivity. Multiband superconductivity unlike single-band superconductivity opens up a paradigm beyond Anderson's theorem to understand the interplay of superconductivity with disorder.

We have applied our methodology to study the effect of substitutional disorder on non-collinear magnetism in binary alloys to MnPt alloy system in this thesis. However, at present we have kept our spin arrangements fixed at 1Q, 2Q and 3Q spin structures. In future we intend to relax the spin structure as well so that we are able to investigate the stability of some arbitrary spin arrangement for our system. Such spin relaxations has been done for ordered systems[40] and we intend to extend it for disordered alloys.

We also intend to extend our study of non-collinear magnetism for systems with partial disorder. Generally off-stoichiometric alloys exhibit partial disorder in the sense that only some of the sub-lattices of the stoichiometric ordered alloy becomes disordered.

Chapter 7

Achievements

This thesis attempts to understand the effect of confinement and disorder on binary systems. In this direction the first set of studies that we made are on confined binary systems, namely on transition metal nano-alloy and nano-oxide clusters.

We find that the first step to the study of electronic structure of clusters is to device an appropriate methodology for the correct determination of ground state structure as magnetic and all other properties of clusters are strongly correlated with its exact geometric structure and arrangement of atoms. For the alloy clusters the search for the actual ground state geometry is guided by the geometries of the clusters of the constituent pure metals. But for such clusters the ground state search is non-trivial for in such clusters there exists "homotops",i.e., same geometric structure with different arrangement of atoms. For oxide cluster finding the actual ground state geometry itself has been a challenging task since all previous theoretical attempts were largely biased and few experiments on such oxide clusters exist in literature. Using a combination of first principle Born-Oppenheimer molecular dynamics simulation and then force optimization techniques we conducted an extensive and unbiased scan through the potential energy surface to reach the actual ground state structure.

Having successfully determined the ground state for these systems, we see that they show some properties much like bulk, others significantly different from bulk. In MnCo nanoalloy, as the environment is made more Mn-rich the average moment of the Co atoms decreases like bulk.

But unlike bulk the Co-rich alloy clusters are found to be ferromagnetic. The MnO clusters are antiferromagnetic much like bulk but they are found to have unusual two-dimensional structural growth upto clusters containing five MnO units. Infact, the larger sized clusters (containg 6-8 MnO units) are found to have these two-dimensional structures as their geometric units and not the bulk-like cuboidal structures as predicted by some studies.

The next set of studies are on model and real substitutionally disordered binary alloys. Through the studies on model binary alloys we have developed an efficient real-space based approach to study the effect of homogeneous as well as correlated disorder on single-band and multiband superconductivity. Our method can also deal with off-diagonal randomness that is present in alloys where there is local lattice distortion due to size mismatch of the constituents. In future we intend to couple our technique with first-principles band structure calculation methodologies like the tight-binding linear muffin-tin orbital method to study the effect of disorder on superconductivity in real binary alloys.

Finally, we have also developed a formalism by combining the tight-binding linearized muffin-tin orbital method and the recursion methods with augmented space formalism (TB-LMTO-ASR) to study the effect of substitutional disorder on non-collinear magnetism in binary alloys.

Bibliography

[1] Wales David J. and Doye Jonathan P.K. J. Phys. Chem. A **101** , 5111 (1997).

[2] Jellinek J., and Krissinel E.B., in *Theory of Atomic and Molecular Clusters*, edited by J. Jellinek (Springer, Berlin, 1999), pp.277-308.

[3] Kondow T. *Progress in Experimental and Theoretical Studies of Clusters*, edited by Kondow T. and Maufune F. (World Scientific, New York, 2003)

[4] Klabunde K.J., *Free Atoms, Clusters and Nanoscale Particles*, (Academic, New York, 1994); Klabunde K.J., *Nanoscale Materials in Chemistry* (Wiley, New York, 2001).

[5] Andrews M.P. and O'Brien S.C., J. Phys. Chem. **96**, 8233 (1992).

[6] Jellinek J., Faraday Discussions **138**, 11 (2008).

[7] Sun S., Murray C.B., Weller D., Folks L., and Moser A., Science **287**, 1989 (2000).

[8] Sinfelt J.H., *Bimetallic Catalysts. Discoveries, Concepts, and Applications*, (John Wiley & Sons: New York, 1983).

[9] Molenbroek A.M. and Norskov J.K., and Clausen B.S., J. Phys. Chem. B **105**, 5450 (2001).

[10] Hansen P.L., Molenbroek A.M. and Ruban A.V., J. Phys. Chem. B **101**, 1861 (1997).

[11] Shibata T., Bunker B.A., Zhang Z., Meisel D., Vardeman II C.F., and Gezelter J.D., J. Am. Chem. Soc. **124**, 11989 (2002).

[12] Darby S., Mortimer-Jones T.V., Johnston R.L., and Roberts C., J. Chem. Phys. **116**, 1536 (2002).

[13] Ruban A.V., Skriver H.L., and Norskov J.K., Phys. Rev. B **59**, 15990 (1999).

[14] Loo C., Lowery A., Halas N., West J., and Drezek R., Nano Lett. **5**, 709 (2005); Huang X.H., Jain P.K., El-Sayed I.H., and M. A. El-Sayed, Nanomedicine **2**, 681 (2007); Pankhurst Q.A., Connolly J., Jones S.K., and Dobson J., J. Phys. D: Appl. Phys. **36**, R167 (2003); C. C. Berry, and A. S. G. Curtis, J. Phys. D: Appl. Phys. **36**, R198 (2003).

[15] Schröder D. and Schwarz H., Angew. Chem. Int. Ed. Engl. **34** 1973 (1995).

[16] Keesee R.G., Chen B., Harms A.C., Castleman A.W., Jr. Int.J.Mass Spectrom.Ion Processes **123** 225 (1993).

[17] Ehrenreich H. and Schwartz L., *Solid State Physics*, Seitz F.

[18] Faulkner J.S.,*Progress in Materials Science* **27**, 1 (1982).

[19] Bansil A., *Electronic Band Structure and its Applications, Lecture Note Series*, (Springer-Verlag, Heidelberg) 283 (1987).

[20] Prasad R., in *Methods of Electronic Structure Calculations*, Andersen O.K., Kumar V., and Mookerjee A., Eds (World-Scientific, Singapore) 211 (1995).

[21] Soven P., Phys. Rev. B **2**, 4715 (1970).

[22] Datta Abhijit and Mookerjee Abhijit, Int.Journ.Mod.Phys.B **6**, Issue 20 3295 (1992).

[23] Chakrabarti A. and Mookerjee A. Euro. Phys. Journ. B **44**,21 (2005).

[24] Knickelbein M.B., Phys. Rev. Lett. **86**, 5255 (2001).

[25] Knickelbein M.B., Phys. Rev. B **70**, 14424 (2004).

[26] Kabir M., Mookerjee A. and Kanhere D.G., Phys. Rev. B **73**, 224439 (2006).

[27] Kabir M., Kanhere D.G. and Mookerjee A., Phys. Rev. B. **75**, 214433 (2007).

[28] Xu X., Yin S., Moro R. and de Heer W.A., Phys. Rev. Lett. **95**, 237209 (2005).

[29] Knickelbein M.B., J. Chem. Phys. **125**, 044308 (2006).

[30] Datta S., Kabir M., Ganguly S., Sanyal B., Saha-Dasgupta T. and Mookerjee A., Phys. Rev. B **76**, 014429 (2007).

[31] Andersen O.K. and Jepsen O. Phys. Rev. Lett **53** 2571 (1984).

[32] Knickelbein M.B., Phys. Rev. B **75**, 014401 (2007).

[33] Yin S., Moro R., Xu X., de Heer W.A., Phys. Rev. Lett. **98**, 113401 (2007).

[34] Nayak S.K. and Jena P. Phys. Rev. Lett **81**, 2970 (1998).

[35] Nayak S.K. and Jena P. Phys. Rev. B **121**, 644 (1999).

[36] Pederson M.R. and Khanna S.N. Phys. Rev. B (Rap. Commun) **59** R693 (1999)

[37] Kino H.,Wagner L.K. and Mitas L. J. Comp. Theo. Nano. **6** 2583 (2009).

[38] Ziemann Paul J. and Castleman A.W., Jr. Phys. Rev. B **46**, 13480 (1992).

[39] Ghosh S., Das N. and Mookerjee A., Int.J.Mod.Phys. B **13** 723 (1999).

[40] Bergman A., Nordström L., Klautau A.B., Frota-Pessoa S., and Eriksson O., Phys. Rev. B **73**, 174434 (2006).