Pauli susceptibility of A_3C_{60} (A=K,Rb)

F. Aryasetiawan
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany
and Department of Theoretical Physics, University of Lund, Sölvegatan 14 A, S-223 62 Lund, Sweden

O. Gunnarsson
Max-Planck-Institut für Festkörperforschung, D-70506 Stuttgart, Germany

E. Koch and R. M. Martin
Department of Physics, University of Illinois, Urbana, Illinois 61801

(Received 4 December 1996)

The Pauli paramagnetic susceptibility of A_3C_{60} (A=K,Rb) compounds is calculated. A lattice quantum-Monte Carlo method is applied to a multi-band Hubbard model, including the on-site Coulomb interaction U. It is found that the many-body enhancement of the susceptibility is of the order of a factor of 3. This reconciles estimates of the density of states from the susceptibility with other estimates. The enhancement is an example of a substantial many-body effect in the doped fullerenes. [S0163-1829(97)51216-1]

The Pauli paramagnetic susceptibility χ is interesting for several reasons. First, χ is enhanced by many-body effects relative to its value χ_0 for noninteracting electrons, and χ/χ_0 is one measure of the strength of the many-body effects in the system. In the alkali-doped C_{60} compounds A_3C_{60} (A=K,Rb), the Coulomb interaction U between two electrons on the same molecule is large[1] compared with the width W of the partly filled t_{1u} band with typical estimates $U/W \sim 1.5-2.5$.[2] In view of this large ratio, one expects very strong many-body effects for these systems. Up to now, however, there seems to be no unambiguous signature of such strong effects.

Second, χ_0 is related to the density of states $N(0)$ at the Fermi energy, and values of $N(0)$ can be extracted from χ if the enhancement χ/χ_0 is known. $N(0)$ is important for the superconductivity and the electron-phonon interaction λ, since theoretical calculations give $\lambda/N(0)$, while some experimental (e.g., neutron[3] and Raman scattering[4]) estimates give $\lambda N(0)$ and others (e.g., photoemission from C_{60}^- molecules[5]) give $\lambda/N(0)$. The estimate of $N(0)$ is therefore crucial for obtaining values of λ and for our understanding of the superconductivity. Typically, for K_3C_{60}, band structure calculations give $N(0) \sim 6-9$ states/(eV spin).[6–11] Estimates based on the specific heat and the NMR relaxation rate give $N(0) \sim 5-7$ states/(eV spin) (Ref. 12) and $N(0) \sim 7.2$ states/(eV spin),[13] respectively. On the other hand, much larger values $N(0) \sim 10-16$ states/(eV spin) for K_3C_{60} are deduced from the susceptibility,[14–17] if many-body effects are neglected. A substantial many-body enhancement (factor 2–3) for the susceptibility[14] could essentially reconcile these rather different estimates. On the other hand, density functional calculations in the local density approximation (LDA) find that the enhancement is only about a factor of 1.3–1.4.[13] We note that the precise meaning of $N(0)$ (density of states versus density of quasiparticles) depends on the context, as is discussed in detail below.

We have used a lattice quantum-Monte Carlo method[2,18] for calculating the Pauli susceptibility for a multiband Hubbard model of the system. For a small system with four C_{60} molecules, we demonstrate that this method gives an accurate enhancement of the susceptibility. For realistic values of the parameters, the susceptibility is enhanced by about a factor of 3, which essentially reconciles estimates of $N(0)$ based on the susceptibility with other estimates.

In the presence of a small external magnetic field $\mathcal{H}$, the energy of the system can be written as

$$E(\mathcal{M}) = E_0(\mathcal{M}) - \mathcal{M}\mathcal{H} \approx E_{00} + \tfrac{1}{2}\alpha\mathcal{M}^2 - \mathcal{M}\mathcal{H}, \qquad (1)$$

where $\mathcal{M} \equiv -\mu_B(N_\uparrow - N_\downarrow)$ is the magnetic moment of the system, with μ_B being the Bohr magneton and N_σ the number of electrons with spin σ. $E_0(\mathcal{M})$ is the energy of the system with a moment $\mathcal{M}$ in the absence of an external field. Minimizing the energy with respect to $\mathcal{M}$, we obtain the susceptibility

$$\chi \equiv \frac{\mathcal{M}}{\mathcal{H}} = \frac{1}{\alpha}. \qquad (2)$$

In the following we therefore calculate $E_0(\mathcal{M})$ for the interacting and noninteracting ($U=0$) systems, from which we obtain the many-body enhancement χ/χ_0.

We use a multiband Hubbard model of the A_3C_{60} compounds

$$H = \sum_{i\sigma}\sum_{m=1}^{3} \varepsilon_{t_{1u}} n_{i\sigma m} + \sum_{\langle ij\rangle \sigma m m'} t_{ijmm'} \psi^\dagger_{i\sigma m}\psi_{j\sigma m'} + U\sum_i \sum_{\sigma m<\sigma' m'} n_{i\sigma m} n_{i\sigma' m'}, \qquad (3)$$

where the first term describes the threefold degenerate t_{1u} states on the sites i and with orbital (m) and spin (σ) indices. The second term describes the hopping between the sites, and the third term describes the Coulomb on-site interaction. Multiplet effects and the electron-phonon interaction have been neglected. In A_3C_{60}, the C_{60} molecules are pref-

TABLE I. The enhancement of the susceptibility for a model with four C_{60} molecules according to diffusion Monte Carlo (DMC) and exact calculations as a function of the Coulomb energy U. The bandwidth is $W=0.58$ eV.

	χ/χ_0	
U	DMC	Exact
1.0	1.89	1.93
1.25	2.20	2.26
1.50	2.63	2.69

erentially in one of two possible orientations in an essentially random way.[19] We take this into account by having a large cell where each molecule takes one of the two preferred orientations in a random way, and the hopping matrix elements between two molecules take into account the orientations of these two molecules.[20,21]

To calculate the energy of the model in Eq. (3), we use a $T=0$ projection lattice Monte Carlo method, introduced by ten Haaf *et al.*[18] In this method a trial function is constructed from a Slater determinant using a Gutzwiller Ansatz.[22] An approximate ground state is then projected out in a diffusion Monte Carlo (DMC) approach, using a ''fixed node'' approximation. This method has been used to study the condition for a Mott-Hubbard transition in A_3C_{60}.[2]

To test the accuracy of the DMC approach, we have first applied the method to a cluster of four C_{60} molecules. This cluster is so small that we can also obtain the exact solution for the model in Eq. (3) using exact diagonalization. We then calculate the coefficient α in Eq. (1) by considering the energy for $N_\uparrow - N_\downarrow = 0$ and 2. The DMC and exact results are compared in Table I. We can see that the DMC method is quite accurate in this case, and if a similar accuracy is obtained for larger systems, it is quite sufficient.

The enhancement of the susceptibility is sensitive to the density of states (DOS) close to the Fermi energy E_F. For small and intermediate size clusters of C_{60} molecules, the DOS depends on the orientations of the molecules, while for large clusters the DOS rapidly converges. Since we can only treat intermediate size clusters [$\sim(32-64)$ molecules] in DMC, we have therefore chosen orientations that in a one-particle approximation give similar DOS close to E_F as for very large clusters.

In Fig. 1 we show results for the total energy as a function of $\mathcal{M} \sim N_\uparrow - N_\downarrow$ for different values of U. The results can be rather well fitted by parabolas, although the precise parameters of the parabolas have a certain dependence on the range of $\mathcal{M}$ considered. From these slopes we can immediately deduce values of the enhancement χ/χ_0. In Fig. 2 the inverse of the enhancement χ_0/χ is shown. It is immediately clear that the enhancement grows with U and that χ would diverge for U a bit larger than 2 eV, if no other transition (e.g., antiferromagnetic) happened before. Estimates of U are typically in the range 1–1.5 eV, giving an enhancement of the susceptibility by about a factor of 3. Qualitatively, similar results have been obtained for a Hubbard model without orbital degeneracy and in the limit of infinite dimensions.[26]

Within the Hartree-Fock approximation, the susceptibility behaves as

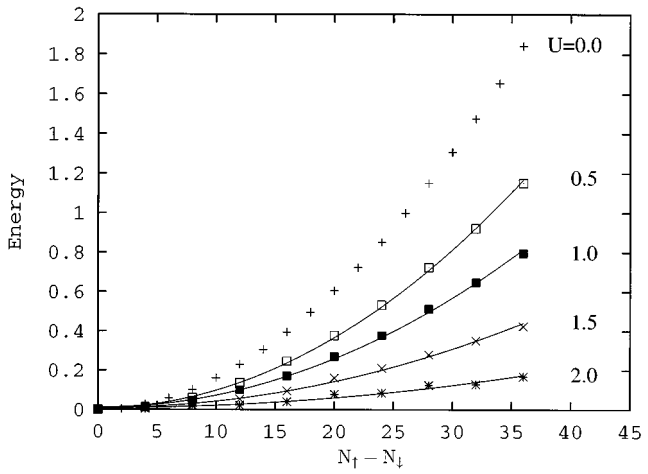

FIG. 1. The energy as a function of $N_\uparrow - N_\downarrow \sim \mathcal{M}$ relative to the energy for $\mathcal{M}=0$. Second order curves have been fitted to the energies. Results for $U=$ 0, 0.5, 1.0, 1.5, and 2.0 eV are shown. The calculations are for 32 molecules and the energy is in eV.

$$\frac{\chi_0}{\chi} \sim 1 - \frac{N(0)}{3} U, \tag{4}$$

where the factor 3 comes from the threefold degeneracy and $N(0)$ is the density of states per spin, which here is about 5.5 states/(eV spin). Here we have assumed that the three orbitals are equivalent. The DMC results show a similar behavior, but with a prefactor in front of U, which is between a factor of 4 and 5 times smaller. This large change in the prefactor illustrates the importance of correlation in these systems.

To deduce $N(0)$ we need to know the Pauli (paramagnetic) susceptibility. Measurements using a superconducting quantum interference device (SQUID) may also contain a diamagnetic contribution, while EPR measurements do not. In Table II we show various experimental results converted to $N(0)$. From the SQUID results, diamagnetic contributions estimated by the respective authors have been subtracted, but the many-body enhancement has *not* been considered. We can see that the results range between 10 and 16 states/(eV spin). If we consider a many-body enhancement of a factor of 3, as deduced above, these results would be reduced to about $N^{susc}(0) \sim 4-5$ states/(eV spin).

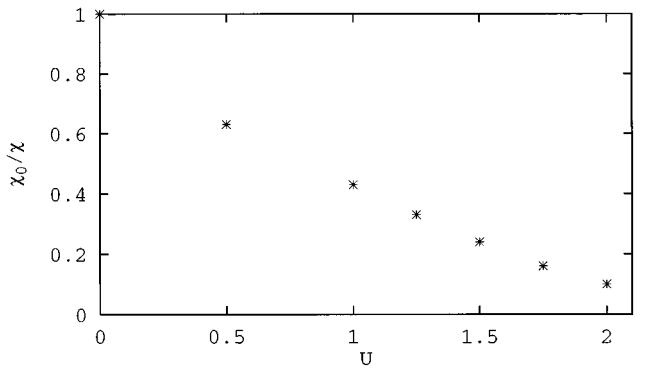

FIG. 2. The inverse enhancement χ_0/χ of the susceptibility for a cluster with 32 molecules as a function of the Coulomb interaction U (in eV). The bandwidth is 0.66 eV.

TABLE II. The density of states $N(0)$ (per eV and spin) for K_3C_{60} as deduced from susceptibility measurements. The results have *not* been corrected for the Stoner enhancement, which would lead to reduced estimates of $N(0)$.

$N(0)$ (K_3C_{60})	Method	Reference
14	SQUID	Ramirez *et al.* (Ref. 14)
16	SQUID	Wong *et al.* (Ref. 15)
11	EPR	Wong *et al.* (Ref. 15)
15	EPR	Tanigaki *et al.* (Ref. 16)
10	EPR	Wang *et al.* (Ref. 17)

Up to now we have not fully considered differences in the definition of the density of states $N(0)$ deduced from different sources. Calculations of the electron-phonon interaction λ are usually based on band structure calculations, giving a density of states $N_0(0)$ for noninteracting electrons. The electron-electron interaction modifies $N_0(0)$ to its interacting value $\mathcal{N}(0)$ (density of quasiparticle states), which should be used in the calculation of λ.[23] This density of states (quasiparticles) enters in the specific heat[24]

$$\frac{C_v}{T} \sim \mathcal{N}(0)(1+\lambda), \tag{5}$$

where the last factor is due to the electron-phonon interaction, assuming that the bandwidth is large compared with the phonon frequency.[25] In the same approximation, the susceptibility can be written as[24]

$$\chi \sim \frac{\mathcal{N}(0)}{1+F_0^a}, \tag{6}$$

where F_0^a is a Landau parameter and $1/(1+F_0^a)$ can be considered as a Stoner enhancement. Our calculation χ/χ_0 includes both the factors $\mathcal{N}(0)/N_0(0)$ and $(1+F_0^a)$. Within the present Monto Carlo technique it is not possible to calculate the specific heat, and, therefore, we cannot separate the two contributions. The value of $N^{susc}(0)$ deduced from the susceptibility, after dividing out many-body effects, should, therefore, primarily be compared with the results obtained from band structure calculations. The band structure calculations have been performed for orientationally ordered systems and give $N_0^{ord} \sim 6-9$ states/(eV spin). Since the real systems have orientational disorder, we estimate the corresponding density of states by solving the Hamiltonian (3) for $U=0$ and orientational disorder. Comparison with calculations for ordered systems suggests a reduction of $N(0)$ by about 15−20 % to $N_0^{disord}(0) \sim 5-7$ states/(eV spin). This is in rather good agreement with $N^{susc}(0) \sim 4-5$ states/(eV spin).

From the specific heat it has been estimated that $\mathcal{N}(0) \sim 5-7$ states /(eV spin) by dividing out the electron-phonon enhancement $(1+\lambda)$.[12] It is interesting that this value is comparable to the noninteracting result $N_0^{disord}(0) \sim 5-7$ states/(eV spin). In contrast to what has been found for the nondegenerate Hubbard model in infinite dimensions,[26] this surprising observation suggests that the enhancement of the density of states is small in the A_3C_{60} compounds or that there may even be a reduction. If this is indeed the case, then the enhancement of the susceptibility would be a Stoner enhancement and the $N_0^{susc}(0)$ obtained from the susceptibility, after dividing out the many-body enhancement, could be compared with other experimental estimates of $N(0)$. We then find that these experimental estimates are essentially brought in line with each other and with the band structure estimates, giving $N(0) \sim 5-7$ states/(eV spin) for K_3C_{60}.

In our model and in the calculations of the susceptibility, we have neglected multiplet effects and the electron-phonon interaction, which are now discussed. The electron-phonon interaction leads to an increase of the density of states at the Fermi energy due to the reduced dispersion of states within roughly a phonon energy of the Fermi energy. This does not influence the susceptibility, if the phonon energies are small compared with the electronic energies.[27] Although this assumption may not be entirely satisfied for A_3C_{60} and interesting effects may result from the finite bandwidth.[28] Here we nevertheless neglect the effects of the electron-phonon interaction on the density of states. Instead we focus on how the electron-phonon interaction influences the moment formation on the C_{60} molecules.

If the multiplets are neglected but the electron-phonon interaction (Jahn-Teller effect) is considered, the lowest spin 1/2 state is favored over the spin 3/2 state, according to calculations for the lowest state of each multiplicity for a free molecule.[29] The energy lowering of the spin 1/2 relative to the spin 3/2 state may be as large as 0.3 eV.[30] This suppresses the formation of moments and probably tends to reduce the susceptibility. On the other hand, the multiplet effects should favor the formation of moments on the C_{60} molecules by giving preference to states with the spin 3/2.

The multiplet effects lead to five spin 1/2 states with the energy $3K$ and three spin 1/2 states with the energy $5K$ relative to the spin 3/2 state. Here K is the exchange integral between two t_{1u} orbitals, and we have assumed that the Coulomb integral U_{xx} between equal orbitals is $2K$ larger than the one (U_{xy}) between different orbitals. To estimate K, we have used a simple model, where the Coulomb integral between two $2p$-charge distributions on two carbon atoms goes as e^2/R, where R is the separation between the two atoms.[31] The on-site interaction was assumed to be 15 eV. Without screening we find that $K=0.12$ eV. An alternative estimate is obtained by using random-phase approximation screening of the Coulomb interaction. We then find $K=0.030$ eV. A similar result (0.024 eV) was also found by Joubert using a density functional approach.[32]

From the numbers above it follows that there should be a partial cancellation between electron-phonon and multiplet effects. Depending on which numbers are used, either effect could be argued to be larger. If the electron-phonon effects win, this may lead to a somewhat smaller enhancement of the susceptibility than was found above (Fig. 2).

We have calculated the Pauli susceptibility of the doped fullerenes A_3C_{60} (A=K,Rb). The enhancement is of the order of a factor of 3, which allows us to reconcile the estimates of the density of states from the susceptibility with other estimates. This suggests that for K_3C_{60} $N(0) \sim 5-7$ states/(eV spin). This value is only slightly smaller than a value [$N(0)=7.2$] used recently to provide support for an

electron-phonon mechanism driving the superconductivity in K_3C_{60},[5] but substantially smaller than some values used in early theoretical discussions. The susceptibility enhancement is appreciably larger than the one (factor 1.3–1.4) found in the LDA, and it is one of the first explicit examples of important many-body effects expected to be found in these systems. Comparison with Hartree-Fock calculations shows, however, that the enhancement is about four to five times smaller than the Hartree-Fock result, illustrating the importance of correlation effects.

[1] R.W. Lof, M.A. van Veenendaal, B. Koopmans, H.T. Jonkman, and G.A. Sawatzky, Phys. Rev. Lett. **68**, 3924 (1992).

[2] O. Gunnarsson, E. Koch, and R.M. Martin, Phys. Rev. B **54**, R11 026 (1996).

[3] K. Prassides, C. Christides, M.J. Rosseinsky, J. Tomkinson, D.W. Murphy, and R.C. Haddon, Europhys. Lett. **19**, 629 (1992).

[4] J. Winter and H. Kuzmany, Phys. Rev. B **53**, 655 (1996).

[5] O. Gunnarsson, H. Handschuh, P.S. Bechthold, B. Kessler, G. Ganteför, and W. Eberhardt, Phys. Rev. Lett. **74**, 1875 (1995).

[6] S.C. Erwin and W.E. Pickett, Science **254**, 842 (1991).

[7] J. L. Martins and N. Troullier, Phys. Rev. B **46**, 1766 (1992).

[8] M.Z. Huang, Y.-N. Xu, and W.Y. Ching, Phys. Rev. B **46**, 6572 (1992).

[9] S. Satpathy, V.P. Antropov, O.K. Andersen, O. Jepsen, O. Gunnarsson, and A.I. Liechtenstein, Phys. Rev. B **46**, 1773 (1992).

[10] D.L. Novikov, V.A. Gubanov, and A.J. Freeman, Physica C **191**, 399 (1992).

[11] V.P. Antropov *et al.* (unpublished).

[12] G.J. Burkhart and C. Meingast, Phys. Rev. B **54**, R6865 (1996).

[13] V.P. Antropov, I.I. Mazin, O.K. Andersen, A.I. Liechtenstein, and O. Jepsen, Phys. Rev. B **47**, 12 373 (1993).

[14] A.P. Ramirez, M.J. Rosseinsky, D.W. Murphy, and R.C. Haddon, Phys. Rev. Lett. **69**, 1687 (1992).

[15] W.H. Wong, M.E. Hanson, W.G. Clark, G. Grüner, J.D. Thompson, R.L. Whetten, S.-M. Huang, R.B. Kaner, F. Diederich, P. Petit, J.-J. Andre, and K. Holczer, Europhys. Lett. **18**, 79 (1992).

[16] K. Tanigaki, M. Kosaka, T. Manako, Y. Kubo, I. Hirosawa, K. Uchida, and K. Prassides, Chem. Phys. Lett. **240**, 627 (1995).

[17] D. Wang, Solid State Commun. **94**, 767 (1995).

[18] D.F.B. ten Haaf, P.W. Brouwer, P.J.H. Denteener, and J.M.J. van Leeuwen, Phys. Rev. B **51**, 353 (1995); H.J.M. van Bemmel, D.F.B. ten Haaf, W. van Saarloos, J.M.J. van Leeuwen, and G. An, Phys. Rev. Lett. **72**, 2442 (1994).

[19] P.W. Stephens, L. Mihaly, P.L. Lee, R.L. Whetten, S.-M. Huang, R. Kaner, F. Deiderich, and K. Holczer, Nature (London) **351**, 632 (1991).

[20] O. Gunnarsson, S. Satpathy, O. Jepsen, and O.K. Andersen, Phys. Rev. Lett. **67**, 3002 (1991).

[21] I.I. Mazin, A.I. Liechtenstein, O. Gunnarsson, O.K. Andersen, V.P. Antropov, and S.E. Burkov, Phys. Rev. Lett. **26**, 4142 (1993).

[22] M.C. Gutzwiller *et al.*, Phys. Rev. **137**, A1726 (1965).

[23] D.J. Scalapino, in *Superconductivity*, edited by R.D. Parks (Dekker, New York, 1969), p. 449.

[24] D. Pines and P. Nozière, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[25] G. Grimvall, *The Electron-Phonon Interaction in Metals* (North-Holland, Amsterdam, 1981), p. 212.

[26] A. Georges, G. Kottliar, W. Krauth, and M.J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).

[27] R.E. Prange and A. Sachs, Phys. Rev. **158**, 672 (1967).

[28] A.I. Liechtenstein, O. Gunnarsson, M. Knupfer, J. Fink, and J.F. Armbruster, J. Phys., Condens. Matter **8**, 4001 (1996).

[29] A. Auerbach, N. Manini, and E. Tosatti, Phys. Rev. B **49**, 12 998 (1994); N. Manini, E. Tosatti, and A. Auerbach, *ibid.* **49**, 13 008 (1994).

[30] O. Gunnarsson, Phys. Rev. B **51**, 3493 (1995).

[31] O. Gunnarsson, D. Rainer, and G. Zwicknagl, Int. J. Mod. Phys. B **6**, 3993 (1992).

[32] D.P. Joubert, J. Phys., Condens. Matter **5**, 8047 (1993).