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LETTER TO THE EDITOR

Local moment formation in disordered systems: a low-filling quasi-atomic limit

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Abstract. Using a self-consistent mean-field approach to a disordered Hubbard model we show that, regardless of the role of correlation in the half-filled band for which the conventional phenomenology is recovered, correlation effects can be strongly enhanced by disorder in the low-filling limit, leading to a well-defined quasi-atomic domain of strong local moments on an inhomogeneous scale. We argue that the theory provides a natural origin for the observed behaviour of the Cs-rich liquid alloys Cu–Au close to stoichiometry.

The interplay between disorder and electron interactions in determining the properties of narrow-band disordered systems has long provoked much study. Correlation effects are usually believed dominant for a half-filled band, diminishing in importance as the filling fraction ν is reduced. But as $\nu \to 0$ in a disordered system, the character of occupied 'tail' states in the band may be dominated by a small fraction of low-energy sites upon which charge is primarily concentrated. Regardless of their role at half-filling, correlation effects may then become important for small ν, leading to a quasi-atomic limit of strong local moments on an inhomogeneous scale.

This possibility is addressed in the present letter by a simple self-consistent mean-field approach to a one-band disordered Hubbard model. The work is motivated by experiments [1, 2] on the Cs-rich liquid alloy $Cs_y[CsAu]_{1-y}$. Near stoichiometry ($y = 0$) the density of states (DOS) of the alloy has been described [3–5] by a two-band model: a lower band primarily generated from 6s states of electronegative Au, and a higher band due mainly to the 6s states of Cs. Charge transfer from Cs to Au is responsible for the ionic character of the liquid which, at stoichiometry, is an ionic insulator with a band gap of ≈ 1.5 eV. As the Cs content increases from stoichiometry the Fermi level moves from the gap into the Cs band and the electrical conductivity increases. However, for relatively small amounts of excess Cs ($y \lesssim 0.07$), strong spin localization is observed [1]; the paramagnetic susceptibility χ is Curie-like and, together with the Cs Knight shift K ($\propto \chi$), is proportional to the concentration y of excess Cs; above $y \sim 0.07$ this behaviour is rapidly lost. The behaviour described is not observed in the crystalline near-stoichiometric alloy, for which no evidence is found for excess localized paramagnetic centres [2]. These features are unlikely to be explained by previous models [3–5] for two reasons: (i) interactions are usually treated in a non-magnetic Hartree–Fock (HF) approximation which *a priori* rules out the possibility of local moments; (ii) charge

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fluctuations are essentially neglected, while their existence in a disordered system can strongly enhance the role of electron correlations.

To clarify the last remark consider (in usual notation) a one-band Hubbard Hamiltonian at the unrestricted HF level

$$H = \sum_{i,\sigma} \varepsilon_{i\sigma} n_{i\sigma} + \sum_{i \neq j,\sigma} V_{ij} C^{+}_{i\sigma} C_{j\sigma} \tag{1}$$

with diagonal disorder in the site energies $\{\varepsilon_i\}$ (and, in general, topological disorder in the $\{V_{ij}\}$). In (1), $\varepsilon_{i\sigma} = \varepsilon_i + U\overline{n_{i-\sigma}}$ is the spin-dependent level shift; the overbar denotes a quantum average for a given disorder realization. The $\{\overline{n_{i\sigma}}\}$ $(i = 1, \ldots N_s)$ must be self-consistently determined, but since $\overline{n_{i\sigma}} \leqslant 1$ we have

$$|\varepsilon_{i\sigma} - \varepsilon_{i-\sigma}| = U|\mu_i| \leqslant U \min[n_i, (2 - n_i)] \tag{2}$$

where $n_i = \overline{n_{i+}} + \overline{n_{i-}}$ is the mean local charge and the equality corresponds to the maximum possible HF local moment $\mu_i = \overline{n_{i+}} - \overline{n_{i-}}$. A large level shift is thus conceivable when $n_i \simeq 1$ but, regardless of the degree of spin polarization, the shift must tend to zero as $n_i \to 0$ or 2. If fluctuations in the charge distribution $\{n_i\}$ were negligible, due e.g. to symmetry in a periodic system, then $n_i \simeq \nu = N_e/N_s$ in (2) (where N_e is the number of electrons in the band) and one indeed expects dominance of correlation effects around half-filling, $\nu = 1$, diminishing as ν is decreased. But as $\nu \to 0$ in a disordered system we envisage the possibility of a quasi-atomic limit with $n_i \simeq 0$ almost everywhere but $n_i \simeq 1$ on a few sites where the consequent interplay between correlation and disorder may generate strong local moments.

To investigate this we use a simple approach incorporating elements of charge and spin fluctuations while regarding the $\varepsilon_{i\sigma}$ for different sites as independent random variables [6]. The (disorder-) averaged site-diagonal σ-spin Green function in which $\varepsilon_{i\sigma}$ is constrained is

$$\overline{G^{\sigma}}(\varepsilon_{i\sigma}; z) = (z - \varepsilon_{i\sigma} - S^{\sigma}(z))^{-1} \tag{3}$$

where, for any single-site theory [7], the self-energy $S^{\sigma}(z) = S^{\sigma}(\overline{G^{\sigma}}(z))$, i.e. it is independent of $\varepsilon_{i\sigma}$ and is a specified function solely of the corresponding fully averaged Green function $\overline{G^{\sigma}}(z)$; a particular choice for $S^{\sigma}(z)$ will later be described and used. $\overline{G^{\sigma}}(z)$ is given by

$$\overline{G^{\sigma}}(z) = \int_{-\infty}^{+\infty} F(\varepsilon_{\sigma}) \overline{G^{\sigma}}(\varepsilon_{\sigma}; z)\, \mathrm{d}\varepsilon_{\sigma}. \tag{4}$$

$F(\varepsilon_{\sigma})$ is the distribution for $\varepsilon_{i\sigma} = \varepsilon_i + \frac{1}{2}U(n_i - \sigma\mu_i)$ which, when specified, closes (3) and (4); the average Green functions then follow, and hence the σ-spin DOS $D_{\sigma}(E) = -(1/\pi)\mathrm{Im}\overline{G^{\sigma}}(E + \mathrm{i}0^{+})$ and Fermi level $E_F \equiv E_F(\nu)$. To mimic the charge distribution in a disordered system we clearly cannot constrain all n_i to the value ν averaged over all sites. In practice, we allow for the possibility of a differential charge on sites with different site energies, but neglect charge fluctuations on sites with the same site energies: for all sites i with $\varepsilon_i = \varepsilon$ we constrain $n_i = n(\varepsilon)$ where $n(\varepsilon)$ is the average charge on these sites. Similarly, for all such sites we constrain μ_i to be $\pm|\mu(\varepsilon)|$ with equal probability, where $|\mu(\varepsilon)|$ is the corresponding mean magnitude of the local moment (the existence or otherwise of which must be determined self-consistently); 'site-differential' on-site spin fluctuations are thus considered. With a given site-energy distribution $f(\varepsilon)$, $F(\varepsilon_{i\sigma})$ $(= F(\varepsilon_{i-\sigma}))$ thus follows. Finally, $n(\varepsilon)$ and $|\mu(\varepsilon)|$ are found self-consistently from (3) and (4) and ($T = 0$ strictly, $kT \ll U$ in practice)

$$n(\varepsilon) = \int_{-\infty}^{E_F} \sum_{\sigma} D^{\sigma}(\varepsilon_{i\sigma}; E)\, \mathrm{d}E \qquad \mu(\varepsilon) = \int_{-\infty}^{E_F} \sum_{\sigma} \sigma D^{\sigma}(\varepsilon_{i\sigma}; E)\, \mathrm{d}E \tag{5}$$

where $D^{\sigma}(\varepsilon_{i\sigma}; E) = -(1/\pi)\mathrm{Im}\overline{G^{\sigma}}(\varepsilon_{i\sigma}; E + \mathrm{i}0^{+})$ and ε_i, μ_i and n_i are constrained respectively to $\varepsilon, \mu(\varepsilon)$ and $n(\varepsilon)$. Equations (3)–(5) enable a complete determination to be made of $n(\varepsilon)$, $|\mu(\varepsilon)|$ and the DOS. To aid interpreting results let $P_{mi}(m = 0,1,2)$ denote the quantum-averaged probability that site i is empty, singly or doubly occupied for a given disorder realization. Conservation of charge and probability give

$$\sum_{m} mP_{mi} = n_i \qquad \sum_{m} P_{mi} = 1.$$

Thus, e.g., $P_{2i} = \overline{n_{i+}n_{i-}}$ $(= \frac{1}{4}(n_i^2 - \mu_i^2)$ in HF) gives a measure of the extent to which electrons are locally correlated; and P_{1i}, P_{0i} follow. As above we obtain the corresponding disorder-averaged functions $P_m(\varepsilon)$ for sites with a given site energy, satisfying analogous conservation rules; e.g. $P_1(\varepsilon) = n(\varepsilon) - 2P_2(\varepsilon)$ and $P_2(\varepsilon) = \frac{1}{4}(n^2(\varepsilon) - \mu^2(\varepsilon))$ give respectively the mean probability that sites of energy ε are singly or doubly occupied. And $P_m = \int f(\varepsilon)P_m(\varepsilon)\, \mathrm{d}\varepsilon$ refers to the average over *all* sites; in particular $P_1 = \nu - 2P_2$ where $\nu = \int f(\varepsilon)n(\varepsilon)\, \mathrm{d}\varepsilon$ follows from (3)–(5).

Insofar as the Au band acts mainly as an electron 'sink', a one-band model is a useful caricature of the Cs-rich alloy $Cs_y[CsAu]_{1-y}$ with $y = \nu$; the diagonal disorder mimics inhomogeneous broadening of the Cs levels due to Coulomb interactions with the disordered distribution of surrounding ions, much as the effect of heavy compensation on the donor impurity levels of a doped semiconductor. For illustration we use [7] $S^{\sigma}(z) = J\overline{G^{\sigma}}(z)$ (as in previous studies of alkali–gold alloys [3–5]), where $J = \langle \Sigma_j |V_{ij}|^2 \rangle$ determines the full bandwidth $W = 4\sqrt{J}$ of the unperturbed semi-elliptic DOS $D_0(E)$ in the limit of no site disorder or interactions ($f(\varepsilon) = \delta(\varepsilon)$, $U = 0$); J is easily related to the site number density and structural properties of the system [7]. For the diagonal disorder we use a normalized cut Lorentzian of halfwidth λ defined (for convenience) for $|\varepsilon| \leqslant W$. The problem is then characterized by three parameters: ν, $\tilde{\lambda} = \lambda/W$, $\tilde{U} = U/W$. For Cs–Au close to stoichiometry, two estimates of $\tilde{U}$ may be inferred from the literature [3–5], $\tilde{U} \simeq \frac{1}{2}$ or 1 (with $W \simeq 0.2$ Ryd).

With $\tilde{U} = \frac{1}{2}$, $\tilde{\lambda} = \frac{1}{4}$ we show in figure 1 the resultant $n(\varepsilon)$, $|\mu(\varepsilon)|$ and the total DOS $D(E) = \Sigma_{\sigma} D_{\sigma}(E)$ for (a) $\nu = 0.01$, (b) $\nu = 0.06$. Defining $\varepsilon(\nu)$ via $\nu = \int^{\varepsilon(\nu)} f(\varepsilon)\, \mathrm{d}\varepsilon$ such that a fraction ν of sites have $\varepsilon \leqslant \varepsilon(\nu)$, we see for low filling ($\nu = 0.01$) a smoothed step function distribution for $n(\varepsilon)$ and $|\mu(\varepsilon)|$ centred on $\varepsilon \simeq \varepsilon(\nu)$. Charge is concentrated mainly on sites with $\varepsilon \lesssim \varepsilon(\nu)$, the smoothing of $n(\varepsilon)$ reflecting the contribution of some sites with higher values of ε to occupied HF pseudoparticle states ($E \leqslant E_F$ in $D(E)$). For $\varepsilon \lesssim \varepsilon(\nu)$, $|\mu(\varepsilon)| \simeq n(\varepsilon)$ corresponding to near-maximum spin polarization: sites with $|\mu(\varepsilon)| = n(\varepsilon)$ are occupied solely by spins of a given type (i.e. only either up or down spin states may overlap a given such site), and $P_2(\varepsilon) = 0$. For $\varepsilon \gtrsim \varepsilon(\nu)$, $|\mu(\varepsilon)|$ falls off rapidly to zero, but $n(\varepsilon)$ is very small and, again, $P_2(\varepsilon) \simeq 0$. For small ν the ground state is thus highly correlated, with $P_2(\varepsilon) \simeq 0\ \forall \varepsilon$. The low-$\nu$ step-function-like behaviour of $n(\varepsilon)$ and $|\mu(\varepsilon)|$ can be regarded as a quasi-atomic limit: physicaliy, $\varepsilon(\nu)$ is the Fermi level for sufficiently low filling in the atomic limit ($D_0(E) = \delta(E)$, $\tilde{\lambda} \neq 0 \neq \tilde{U}$) when all sites are either singly occupied or empty ($P_2(\varepsilon) = 0\ \forall \varepsilon$) with $n(\varepsilon) = 1 = |\mu(\varepsilon)|$ for $\varepsilon < \varepsilon(\nu)$ and zero otherwise. Note that for $\varepsilon < \varepsilon(\nu)$ in the strict atomic limit, $|\mu(\varepsilon)| = n(\varepsilon)$ implies $P_2(\varepsilon) = 0$; hence $P_1(\varepsilon) = n(\varepsilon) = 1$, $P_0(\varepsilon) = 0$. For the quasi-atomic limit found above, $|\mu(\varepsilon)| \simeq n(\varepsilon)$ for $\varepsilon \lesssim \varepsilon(\nu)$ again implies $P_2(\varepsilon) \simeq 0$; hence $P_1(\varepsilon) \simeq n(\varepsilon)$, $P_0(\varepsilon) \simeq 1 - n(\varepsilon)$. Now, however, $n(\varepsilon)$ is somewhat less than unity for the low-ε sites (see figure 1),

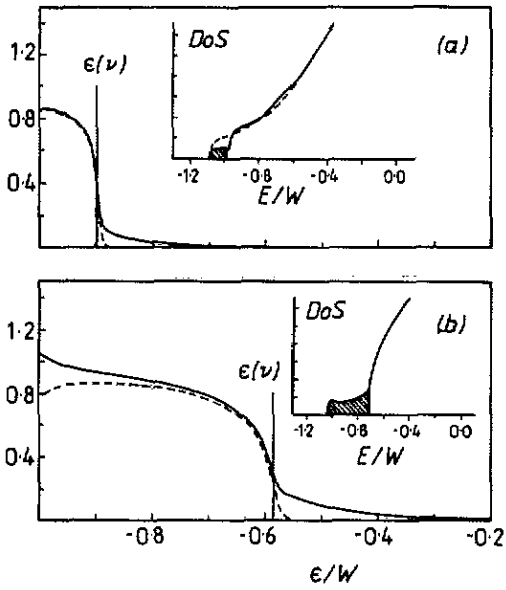

Figure 1. $n(\varepsilon)$ (full curve) and $|\mu(\varepsilon)|$ (broken curve) as a function of ε/W, and the corresponding densities of states $D(E)$ versus E/W, for $\tilde{U} = \frac{1}{2}$, $\tilde{\lambda} = \frac{1}{4}$ with (*a*) $\nu = 0.01$, (*b*) $\nu = 0.06$. The energy $\varepsilon(\nu)$ is marked on the charge–moment plots; occupied states in $D(E)$ are shaded. In (*a*) the non-interacting ($\tilde{U} = 0$) $D(E)$ is shown for comparison (broken curve).

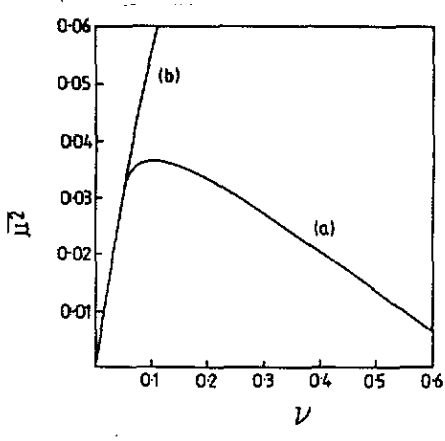

Figure 2. $\overline{\mu^2}$ versus ν for $\tilde{\lambda} = \frac{1}{4}$ with (*a*) $\tilde{U} = \frac{1}{2}$, (*b*) $\tilde{U} = 1$.

reflecting the fact that while charge is concentrated primarily on such sites, they have a non-vanishing probability of being unoccupied; $P_0(\varepsilon) > 0$. The quasi-atomic limit is also reflected in the 'step' in $D(E)$ at $E \simeq E_F$, seen in figure 1(*a*) where the non-interacting ($\tilde{U} = 0$) DOS is shown for comparison. For $0 < \nu \lesssim \nu_c$ the above behaviour persists, where $\nu_c \simeq 0.08$ is such that $\varepsilon(\nu_c) = -W/2$ i.e. coincides with the lower edge of the unperturbed band $D_0(E)$. A tiny fraction of sites with low values of ε begin to be doubly occupied as $\nu \to \nu_c$, but for the vast majority of sites, with $\varepsilon \lesssim \varepsilon(\nu)$, charge and spin remain strongly coupled ($|\mu(\varepsilon)| \simeq n(\varepsilon)$, $P_2(\varepsilon) \simeq 0$) with step-function-like distributions centred on $\varepsilon \simeq \varepsilon(\nu)$. In this domain of strongly localized spins, we expect [8]

$$kT\chi \simeq \mu_0 \mu_B^2 N_s^{-1} \sum_i \langle\langle (n_{i+} - n_{i-})^2 \rangle\rangle$$

for experimentally relevant temperatures, which yields $kT\chi = \mu_0 \mu_B^2 P_1$. For $\nu \lesssim \nu_c$ we find the mean probability of double occupancy $P_2 \sim O(\nu^2)$; hence the mean probability of single occupancy $P_1 = \nu$ to $O(\nu^2)$, and a free spin-$\frac{1}{2}$ Curie law susceptibility results.

The filling fraction ν_c represents a crossover in qualitative behaviour. For $\nu \gtrsim \nu_c$ charge and spin increasingly decorrelate, the quasi-atomic $n(\varepsilon)$, $|\mu(\varepsilon)|$ distributions break up, and the local moments progressively weaken. This is made evident from figure 2 showing $\overline{\mu^2}$ versus ν for $\tilde{U} = \frac{1}{2}$, $\tilde{\lambda} = \frac{1}{4}$ where $\overline{\mu^n} = \int f(\varepsilon)|\mu(\varepsilon)|^n \, d\varepsilon$. For $\nu \lesssim \nu_c$, $\overline{\mu^2}$ is essentially linear in ν reflecting a step-function-like $|\mu(\varepsilon)|$ distribution. For $\nu > \nu_c$ this quasi-atomic limit behaviour is lost rapidly, and $\overline{\mu^2}$ drops steadily to zero at $\nu = \nu_0 \simeq$ 0.6–0.7 above which moments are no longer stable. For $\nu = 1$ there are thus no local

moment instabilities, but as $\nu \rightarrow \nu_0+$ the first such appear; as ν decreases further moments progressively stabilize, and for $\nu \lesssim \nu_c$ quasi-atomic behaviour is reached.

The above is for $\tilde{U} = \frac{1}{2}, \tilde{\lambda} = \frac{1}{4}$. As $\tilde{U}$ is increased, $\nu_0 \rightarrow 1$: local moments exist at half-filling, reflected in a pseudogap in $D(E)$ which deepens as $\tilde{U}$ increases. (In particular, the choice $\tilde{U} = 1$ (with $\tilde{\lambda} = \frac{1}{4}$) would produce strong moments for all ν, although for $\nu \lesssim 0.08$ this has little effect on, e.g., $\overline{\mu^2}$: see figure 2.) For small filling the disorder parameter $\tilde{\lambda}$ essentially determines the ν_c at which quasi-atomic behaviour sets in, ν_c decreasing with $\tilde{\lambda}$—e.g. $\nu_c = 0.02$ for $\tilde{\lambda} = 0.05$, $\tilde{U} = \frac{1}{2}$. In contrast, provided λ is not comparable to W, the half-filling limit is not particularly sensitive to $\tilde{\lambda}$. For suitably small $\tilde{\lambda}$, and with $\tilde{U}$ in excess of that required to produce moments at $\nu = 1$, we find that $\overline{\mu}/\nu$ ($\equiv N_e^{-1}\langle\Sigma_i|\mu_i|\rangle$) initially decreases as ν drops from 1. In this sense, half-filling is optimal for local moment formation and our results are in accord with recent important calculations by Milovanović *et al* [9] on the disordered Hubbard model. But as ν is decreased further, $\overline{\mu}/\nu$ eventually increases to a value of order 1 as $\nu \rightarrow \nu_c$ and the low-filling quasi-atomic limit is again reached for $\nu \lesssim \nu_c$ where occupied states in $D(E)$ are associated mainly with low-energy sites with strong local moments.

The theory provides a natural origin for the observed behaviour of liquid $Cs_\nu[CsAu]_{1-\nu}$. Starting from stoichiometry ($\nu = 0$), E_F moves into the lower edge of the Cs band ($D(E)$) as ν increases. For $0 < \nu \lesssim \nu_c$ ($\simeq 0.08$ with $\tilde{U} = \frac{1}{2}$, $\tilde{\lambda} = \frac{1}{4}$) the interplay between correlation and disorder produces strong local moments with a free spin-$\frac{1}{2}$ Curie law χ (and hence K) proportional to ν, as observed [1] for $0 < \nu \lesssim 0.07$ together with an enhanced spin–lattice relaxation rate T_1^{-1} characteristic of strongly localized spins. As ν increases above $\simeq 0.07$ the quasi-atomic limit evident in the behaviour of K and T_1^{-1} is rapidly lost, commensurately with the above findings. In addition, and consequent upon the concentration of charge on 'Coulombically favourable' low-ε Cs ions, the local ionic environment may distort to accommodate the charge, leading to a potential role for polaronic processes as suggested in [1], the importance of which would naturally diminish as ν exceeds ν_c and the charge encompasses a larger fraction of the available sites.

Disorder is also responsible for the localized or extended nature of the pseudoparticle states. Although localization *per se* is not addressed here, it would seem unlikely that sites associated with strong local moments are overlapped solely by extended states, and the presence of a low-energy tail of localized states in the Cs band may underlie the small observed [1] thermal gap for electron–hole pair generation around stoichiometry, compared with a larger optical gap. There is no direct connection between the nature of states at E_F and the persistence of on-site local moments (which reflect all occupied states overlapping a site), and it is known [9] that local moment instabilities may occur when states at E_F are extended. But as E_F moves further into the Cs band with increasing ν, one expects pseudoparticle states at E_F to become less strongly localized and ultimately extended, with an evolution to conventional band-like states as $\nu \rightarrow 1$ where the resultant pure Cs reached in the alloy experiments is a high-density, uncorrelated, clean metal. As described elsewhere [10] the theory also rationalizes the observed behaviour of pure Cs upon subsequent expansion to lower densities along the liquid–gas coexistence curve [11]. This corresponds to increasing $\tilde{U}$ (decreasing W and increasing U in general). For low $\tilde{U}$ we have the uncorrelated clean metal. As $\tilde{U}$ increases local moments stabilize and a pseudogap containing E_F appears in $D(E)$, which progressively deepens until states at E_F become localized and an Anderson–Mott–Hubbard transition occurs to a correlated insulator with local moments.

In summary, we have shown that at low filling, disorder can substantially enhance the role of correlations, leading to strong-quasi-atomic local moments on an inhomogeneous scale, regardless of the role of correlation at half-filling. We believe such behaviour may be manifest in the liquid alloys Cs–Au close to stoichiometry.

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References

[1] Dupree R, Kirby D J, Freyland W and Warren Jr W W 1980 *Phys. Rev. Lett.* **45** 130
[2] Dupree R, Kirby D J and Warren Jr W W 1980 *Phys. Rev.* B **31** 5597
[3] Franz J R, Brouers F and Holzhey C 1980 *J. Phys. F: Metal Phys.* **10** 235
[4] Holzhey C, Brouers F and Franz J R 1981 *J. Phys. F: Metal Phys.* **11** 1047
[5] Holzhey C, Brouers F, Franz J R and Schirmacher W 1982 *J. Phys. F: Metal Phys.* **12** 2601
[6] The method is essentially a generalization, to include site disorder, of Cyrot M 1972 *Phil. Mag.* **25** 1031
[7] Logan D E and Winn M D 1988 *J. Phys. C: Solid State Phys.* **21** 5773
[8] Bartel L C and Jarrett H S 1974 *Phys. Rev.* B **10** 946
[9] Milovanović M, Sachdev S and Bhatt R N 1989 *Phys. Rev. Lett.* **63** 82
[10] Logan D E 1991 *J. Chem. Phys.* **94** 628
[11] See, e.g.
Freyland W and Hensel F 1985 *The Metallic and Nonmetallic States of Matter* eds P P Edwards and C N R Rao (London: Taylor and Francis)