CAMBRIDGE

Cambridge University Press
978-1-107-41007-7 - Materials Research Society Symposium Proceedings: Volume 193: Atomic Scale Calculations of Structure in Materials
Editors: Murray S. Daw and Michael A. Schlüter
Excerpt
More information

PART I

Electronic and Structural Properties

Cambridge University Press
978-1-107-41007-7 - Materials Research Society Symposium Proceedings: Volume 193: Atomic Scale Calculations of Structure in Materials
Editors: Murray S. Daw and Michael A. Schlüter
Excerpt
More information

Cambridge University Press
978-1-107-41007-7 - Materials Research Society Symposium Proceedings: Volume 193: Atomic Scale Calculations of Structure in Materials
Editors: Murray S. Daw and Michael A. Schlüter
Excerpt
More information

ON THE DYNAMICAL SPIN SUSCEPTIBILITY OF PARAMAGNETIC La_2CuO_4

H. WINTER*, Z. SZOTEK** AND W.M. TEMMERMAN**
*Kernforschungszentrum Karlsruhe, INFP, P.O. Box 3640, D-7500 Karlsruhe, Federal Republic of Germany
**SERC Daresbury Laboratory, Warrington WA4 4AD, United Kingdom

ABSTRACT

The self-consistent one-electron wave functions and energy bands obtained by the LMTO-ASA method within the local density approximation (LDA) are used to calculate the wave vector and frequency dependent non-interacting spin susceptibility of paramagnetic La_2CuO_4 in the body-centred tetragonal (bct) structure. We show that the tendency towards the antiferromagnetic instability is strongly dependent on the effects of the matrix elements which lead to a substantial depression of the susceptibility, especially near the X-point. The Fermi surface nesting properties, although important for the susceptibility, are by far not sufficient for the instability and the interband transitions turn out to be of great significance. Our results indicate that the susceptibility is at least 3 times too small to drive this system through a transition to the antiferromagnetic state, and we discuss possible reasons for this failure.

INTRODUCTION

Local spin density (LSD) calculations have indicated that La_2CuO_4 might be close to the experimentally established antiferromagnetic groundstate [1], however there have been no serious predictions of a strong local moment [2-7]. In our LSD studies [6,7] we have noticed that the value of the moment has been strongly dependent on the number of k-points and the basis sets used, and the bands corresponding to different values of the moment have been characterized by a different degree of hybridization between Cu d and O p states. In particular, in the course of iterations towards self-consistency there has occurred a state, characterized by relatively well localized Cu d bands with the magnetic moment of 0.35 μ_B (Bohr magneton), and associated with a considerable semiconducting gap, which has however decayed slowly into a paramagnetic state. This has motivated us to study the linear response of the electron spins, in an assumed paramagnetic ground state of La_2CuO_4 in the bct structure, to the wave vector $\vec{q}$- and frequency ω- dependent magnetic field. In analogy to systems like Ni or Fe a transition to a magnetic state should be signalized through the fulfilment of the Stoner criterion by the static spin susceptibility, $\tilde{\chi}_S$, at the appropriate wave vector $\vec{q}$ (X-point in the case of La_2CuO_4). Alternatively, as it was previously discussed for systems like Pd, V [8,9] or Ni_3Ga [10], the magnitude of $\tilde{\chi}_S$ should tell us how far away from a magnetic transition the system is from the LDA point of view.

The spin susceptibility of La_2CuO_4 was previously calculated by Xu et al [11], and Leung et al [3] performed similar calculation for Sc_2CuO_4. However, these authors were in particular interested in studying a Fermi surface (FS) driven instability. They evaluated a quantity called the static generalized susceptibility, which contained only the contributions from the intraband transitions. Since, due to the Fermi criterion the intraband contributions are provided by the bands crossing the Fermi level E_F in various parts of the Brillouin zone

Cambridge University Press
978-1-107-41007-7 - Materials Research Society Symposium Proceedings: Volume 193: Atomic Scale Calculations of Structure in Materials
Editors: Murray S. Daw and Michael A. Schlüter
Excerpt
More information

(BZ), in these calculations only the Cu $d_{x^2-y^2}$ - O $p_{x,y}$ antibonding band (band 17) was considered. In both calculations the susceptibility has a peak at the X-point which bears some significance in that it coincides with the ordering wave vector of the antiferromagnetic state, just as it would be expected for the FS driven instability. However, their work does not address itself to the importance of other bands or an influence of the matrix elements on the susceptibility, and does not investigate whether there are other mechanisms, besides the nesting, to drive the magnetic instability.

In contrast to [3,11] in our calculation of the spin susceptibility we have considered transitions between the 54 lowest bands. Combined with this we have included the appropriate matrix elements, determined by the Bloch states involved in a particular transition, providing a weighting of the susceptibility according to angular momentum symmetry and also with respect to chemical species. The matrix elements are especially crucial for assessing the tendency towards a magnetic instability. It is a decomposition of the susceptibility with respect to pairs of sites within the unit cell which proves particularly useful for a judgement on how far away from a magnetic instability the system is, and whether a local instability could be possible. The other useful decomposition is the one with respect to the bands. One can study the contributions from each occupied band separately, after summing over all unoccupied states.

For the present calculation we have extended our first principles formalism derived within the LSD-RPA for paramagnetic transition metals [12,9] to the case of complex systems with many atoms per unit cell. For the non-interacting susceptibility, χ_s^P, this means to be able to deal with a considerable increase in the number of possible transitions between the occupied and unoccupied one-electron states. Details concerning this point and the relevant formulae are given in [13].

To obtain the non-interacting spin susceptibility, χ_s^P, the one particle Green's function is needed, and we use the self-consistent LMTO-ASA wave functions and energy bands to determine it. All the necessary information on the band structure underlying the present susceptibility calculation can be found in [6,13].

The quantity which we are concerned with in this work is the diagonal part of the real space double Fourier transform, $\tilde{\chi}_s^P(\vec{q},\vec{q},\omega)$, of the non-interacting spin susceptibility χ_s^P. It can be written as a sum over the contributions from all possible pairs of atomic sites in the unit cell, and a sum over all transitions from the occupied to unoccupied states, integrated over the Brillouin zone.

In the next section we shall discuss the $\vec{q}$ and ω dependence of the spin susceptibility, $\tilde{\chi}_s^P$, for La_2CuO_4, as obtained in the present calculation. We shall also extract from our calculations the generalized susceptibility, as evaluated in [3,11], to stress the differences between the present approach to the studies of the susceptibility and the other calculations.

RESULTS AND DISCUSSION

Let us start from discussing the intraband contributions to the susceptibility in the context of the matrix elements' effects and in comparison with the interband contributions. This bears directly upon the question whether the failure of LSD in obtaining the antiferromagnetic groundstate of La_2CuO_4 is due to an inadequacy of describing the nesting of the FS, or is related to the degree of hybridization of the Cu d bands with the O p bands. Although the importance of the nesting for the susceptibility was strongly argued in [3,11], the influence of the matrix elements was not studied. That the effects of matrix elements are very important can be seen in Figure1. There we have shown the contributions from the

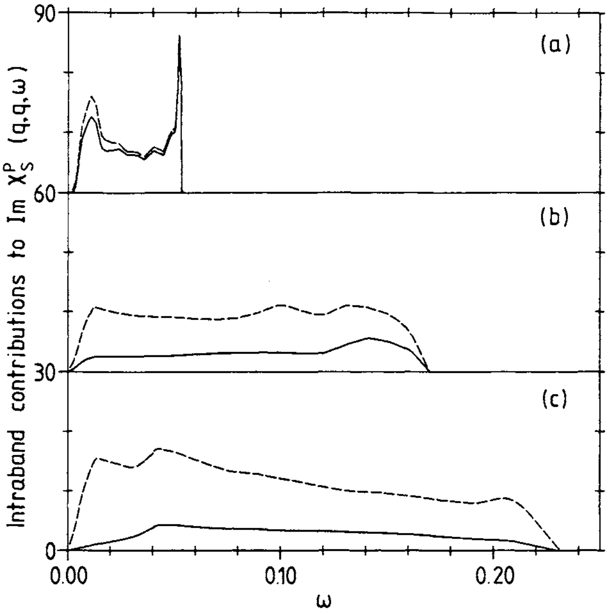

Fig. 1. The contributions of band 17 to the imaginary part of the non-interacting dynamical spin susceptibility including (solid line) and ignoring (dashed line) the matrix elements' effects for the wave vectors $\vec{q}$: (a) (0.075, 0.75, 0), (b) (0.25, 0.25, 0), and (c) (0.5, 0.5, 0), all in dimensionless units (du).

intraband transitions to the imaginary part of the dynamical spin susceptibility for several values of $|\vec{q}|$ along the (1,1,0) direction. The comparison is between the quantities including the matrix elements and the relevant contributions obtained in the case when the matrix elements have been set equal to 1. Due to the normalisation of the Bloch wave functions the value 1 for the matrix elements is reached in the limit of $|\vec{q}| \rightarrow 0$. However, on increasing $|\vec{q}|$ the values of the matrix elements decrease, becoming increasingly effective in depressing the susceptibility. This remains true irrespectively whether the intraband transitions link states near to E_F (low frequency part in Figure 1) or regions more distant from E_F (high frequency part in Figure 1). These features are intimately connected with the large width and significant Cu d - O p hybridization of band 17, as found in the band structure calculations. Striking are also the marked changes in the shapes of the curves as a function of $|\vec{q}|$. Moreover, the frequency range, $\Delta\omega(\vec{q})$, of the imaginary part of $\tilde{\chi}_S^P$ is strongly dependent on $|\vec{q}|$, increasing from about 0.05 Ryd at $\vec{q} = (0.075, 0.075, 0)$ (d.u) to about 0.23 Ryd at the X-point.

As a consequence of the orthogonality of the Bloch coefficients at any given $\vec{k}$-point in the BZ the interband transitions do not contribute to the imaginary part of the susceptibility at $|\vec{q}| = 0$. However, they reach sizable values at the finite $|\vec{q}|$'s. Depending on the combination of bands involved in a particular transition, of which we have considered the combinations of the 17 lowest occupied bands with the bands from 17 to 54, the contributions to the imaginary part of $\tilde{\chi}_s^P$ come from various frequency regions, which extend up to 2.8 Ryd. We have noticed that as a function of frequency, the interband contributions to the imaginary part of the spin susceptibility are sharply structured, in comparison with the intraband contributions, and depending on the frequency range may have non-negligible amplitudes. In fact, due to the flatness of some of the band complexes involved in the transitions, some of the contributions could get enhanced by a factor of up to a few hundreds, if the matrix elements were ignored. In particular, the importance of the interband transitions increases with $\vec{q}$ approaching the BZ boundary. Also the values of the interband contributions are highly dependent on the wave function overlap between the $\vec{k}$-points separated by $\vec{q}$, and this overlap can be especially large for more localized states.

A more quantitative analysis of the importance of the interband transitions is given in Table I. There we have collected the most important results of our studies, with respect to the static part of the $\vec{q}$-dependent spin susceptibility, obtained with the help of the Kramers-Krönig relations on the basis of the imaginary part of the non-interacting dynamical spin susceptibility. The static $\vec{q}$-dependent spin susceptibility (see column 2) for several values of $|\vec{q}|$ along the (1,1,0) direction is decomposed into the contributions from the intraband transitions (see column 3), and the contributions from all other transitions (column 4). For completeness and comparison with the results of [3,11] we have also presented our values for the generalized spin susceptibility (see column 5), which are simply the intraband contributions to the susceptibility obtained for the matrix elements set equal to unity. Our generalized susceptibility, reaching its maximum at the X-point, is very close to the one calculated by [11], but somewhat higher than the result of [3] for Sc_2CuO_4. However, after including the matrix elements the behaviour of the generalized susceptibility gets reversed, and the maximum occurs at the Γ-point, instead of the X-point (compare columns 3 and 5). This shows that although the FS nesting is important for the susceptibility it is by far not sufficient for the antiferromagnetic instability. In fact, on approaching the BZ boundary the $\vec{q}$ dependence of the static non-interacting susceptibility is dominated by the interband contributions (compare columns 2 and 4) which in this region are much larger than the intraband contributions (column 3). The reason is that the matrix elements have a devastating effect on the intraband contributions in the region of large $|\vec{q}|$'s, and a combined effect of the matrix elements on both the intra- and interband contributions is to smooth out the peak at the X-point, thus reducing the tendency towards the antiferromagnetic instability.

Table I. Static non-interacting susceptibility for some $\vec{q}$-vectors in (1,1,0) direction.

$\vec{q}$	$\tilde{\chi}_s^P(\vec{q},\vec{q},0)$	Contribution to $\tilde{\chi}_s^P(\vec{q},\vec{q},0)$ from intraband transitions	Contribution to $\tilde{\chi}_s^P(\vec{q},\vec{q},0)$ from interband transitions	Intraband transitions contribution ignoring matrix elements
(0,0,0)	15.800	15.800	0.000	15.800
(0.075,0.075,0)	20.001	13.944	6.057	17.100
(0.25,0.25,0)	24.859	6.560	18.299	22.500
(0.5,0.5,0)	26.569	5.670	20.899	34.500

Table II. Contributions of pairs of the chemical components to the static non-interacting susceptibility for wave vector $\vec{q} = (0.5,0.5,0)$ du.

Component	La-sites	Cu-site	in plane O-sites	apex O-sites
La-sites	5.730	- 0.122	- 0.031	- 0.696
Cu-site	- 0.122	10.630	0.420	- 0.209
in plane O-sites	- 0.031	0.420	5.970	- 0.073
Apex O-sites	- 0.696	- 0.209	- 0.073	5.670

Following the earlier remarks concerning the usefulness of the decomposition of the spin susceptibility with respect to the chemical components, in Table II we have collected the contributions of pairs of atomic sites in the unit cell to the susceptibility. The corresponding numbers have been obtained as a result of a partial summation over the sites belonging to the same chemical component and occupying equivalent positions. Again, they indicate the importance of the interband contributions which imply bands of varying character, because - unlike in the case of band 17 - appreciable weights appear at the La - and the apex O- sites. The largest contribution, however, is still due to the Cu-atom. Owing to the fact that the site off diagonal terms are relatively small one can use the following criterion

$$1 - \tilde{\chi}_s^{P,\tau\tau}(\vec{q},\vec{q},0) \cdot \bar{K}^{\tau} = 0 \qquad (1)$$

to judge about the possible instability. Here $\tilde{\chi}_s^{P,\tau\tau}$ is the site decomposed non-interacting static spin susceptibility, as quoted in Table II, and $\bar{K}^{\tau}$ can be interpreted as some site-dependent scalar average over the angular momentum matrix elements of the exchange and correlation enhancement potential, defining the kernel of the integral equation for the fully interacting susceptibility χ_s. Table II suggests that, if at all, the instability should occur at the Cu-site. Assuming for $\bar{K}^{Cu}$ a value of the order of 0.03 Ryd [14] we find that the product of $\tilde{\chi}_s^{P,CuCu} \cdot \bar{K}^{Cu}$ is too small by at least a factor of 3 to indicate the instability. The inclusion of still more interband transitions is unlikely to change the argument relevantly. However, it seems that more localized and less hybridized Cu d bands could give rise to the magnetic instability by increasing the interband contributions. In particular, we envisage that the Cu t_{2g} states need to be more localized, and this could be achieved through an inclusion of the self-interaction correction (SIC) into the LDA [15,5]. In the Cu partial densities of states of La_2CuO_4 [16] the e_g states, strongly hybridizing with the O p states, extend over a wide energy range, whilst the t_{2g} states are confined to a much narrower energy region. The hope is, that the SIC to the LDA will further localize these t_{2g} states, whilst leaving the band-like e_g states essentially untouched. As a consequence, these more localized t_{2g} states would give rise to an increase of their interband contributions to the spin susceptibility by increasing the wave function overlap, through decreasing the variation of the wave function coefficients in the Brillouin zone. As a result, this increase in the interband contributions would eventually lead to the antiferromagnetic instability.

CONCLUSIONS

In this first principles study of the non-interacting dynamical spin susceptibility of La_2CuO_4 we have shown that the tendency towards the antiferromagnetic instability is a very complex phenomenon, strongly dependent on the combined effects of the FS nesting, interband transitions, matrix elements and the electronic exchange and many-body correlations. With respect to the many-body enhancement, we have concluded that the susceptibility is at least 3 times too small for the antiferromagnetic instability. Similar conclusions have been reached by [5], and for Sc_2CuO_4 by [3], through numerically applying a staggered magnetic field in a supercell calculation. The authors of [5] conclude that the enhancement is at least a factor of 5 too small to account for the antiferromagnetic instability, while in [3] a factor of 2 has been obtained. We consider both results to be consistent with our estimate of 3.

It has become clear that the antiferromagnetic groundstate is strongly coupled to the degree of hybridization of the Cu d and Op bands, and for the LDA band structure, underlying the present susceptibility studies, this degree is especially high, as also indicated by the spin part of the magnetic form factor approximately evaluated in our work [13]. More localized and less hybridized bands are needed to increase the tendency towards the antiferromagnetic instability, by changing the characters of the Bloch states coefficients, and also due to band narrowing. The interband transitions, which turn out to be so significant, in comparison with the FS nesting, are strongly dependent on the matrix elements and could increase substantially due to smaller variation of the wave function coefficients throughout the BZ. This is consistent with the observation made in the course of the spin polarized iterations towards self-consistency [6,7]: the higher the magnetic moment of the intermediate state the more pronounced was the Cu-3d character of the corresponding bands, and a slow decrease of the magnetic moment on the Cu-site was coupled to the increase of the Cu d and Op hybridization, eventually ending up in the state characterized by the paramagnetic band structure, consistently with the present susceptibility calculation.

REFERENCES

1. A. Aharony, R.J. Birgeneau, A. Coniglio, M.A.Kastner and H.E. Stanley, Phys. Rev. Lett. 60, 1330 (1988).
2. W.E. Pickett, Rev. Mod. Phys. 61, 433 (1989).
3. T.C. Leung, X.W. Wang and B.N. Harmon, Phys. Rev. B 37, 384 (1988).
4. P.A. Sterne and C.S. Wang, Phys. Rev. B 37, 7472 (1988).
5. J. Zaanen, J. Jepsen, O. Gunnarson, A.T. Paxton and O.K. Andersen, Physics C 153-155, 1636 (1988).
6. G.Y. Guo, W.M. Temmerman and G.M. Stocks, J. Phys. C 21, L103 (1988).
7. W.M. Temmerman, Z. Szotek and G.Y. Guo, J. Phys. C 21, L867 (1988).
8. E. Stenzel and H. Winter, J.Phys. F 16, 1789 (1986).
9. E. Stenzel, H. Winter, Z. Szotek and W.M. Temmerman, Z. Phys. B 70, 173 (1988).
10. H. Winter, Z. Szotek and W.M. Temmerman, Solid State Commun. 1990 (in press).
11. J.-H. Xu, T.J. Watson-Yang and A.J. Freeman, Phys. Lett. A 120, 489 (1987).
12. E. Stenzel and H. Winter, J. Phys. F 15, 1571 (1985).
13. H. Winter, Z. Szotek and W.M. Temmerman, Z. Phys. B 1990 (in press).
14. V.L. Moruzzi, J.F. Janak and A.R. Williams, Calculated Electronic Properties of Metals, (Pergamon Press Inc., New York, 1978), p.96.
15. R.O. Jones and O. Gunnarsson, Rev. Mod. Phys. 61, 689 (1989).
16. W.M. Temmerman, P.A. Sterne, G.Y. Guo and Z. Szotek, Molecular Simulation 4, 153 (1989).

FIRST–PRINCIPLES INTERATOMIC POTENTIALS FOR TRANSITION METALS AND THEIR SURFACES

JOHN A. MORIARTY* AND ROBERT B. PHILLIPS**
*Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550
**Sandia National Laboratories, Livermore, CA 94550

ABSTRACT

For bulk transition metals, a first–principles generalized pseudopotential theory (GPT) of interatomic potentials has been developed in which the cohesive–energy functional takes the form of a volume term plus sums over widely transferable two–, three–, and four–ion potentials. The GPT has been further extended to surfaces by making an internal transformation of this functional to an embedded–atom–like format in which the embedding function is identified as the bulk volume term and the atomic volume is replaced by an average electron density. Applications of the bulk and surface GPT to the calculation of structural, vacancy–formation, and surface energies in Cu and Mo, and to the investigation of surface relaxation and reconstruction in Mo are discussed.

INTRODUCTION

A first–principles interatomic–potential expansion of the total energy suitable for transition metals has recently been obtained [1] within the framework of generalized pseudopotential theory (GPT) [1–3] and local–density quantum mechanics [4]. In the bulk elemental metal with atomic volume Ω, the cohesive–energy functional takes the form

$$E_{coh}(\mathbf{R}_1 \ldots \mathbf{R}_N) = E_{vol}(\Omega) + \frac{1}{2N}\sum_{i,j}{}' v_2(ij) + \frac{1}{6N}\sum_{i,j,k}{}' v_3(ijk) + \frac{1}{24N}\sum_{i,j,k,l}{}' v_4(ijkl) \,. \quad (1)$$

The leading volume term E_{vol} in this expansion includes all one–ion *intra–atomic* contributions to the total energy and already yields a good estimate of the equilibrium cohesive energy in lowest order. The interatomic potentials v_2, v_3, and v_4 are given in terms of weak pseudopotential and *d*–state tight–binding and hybridization matrix elements coupling different sites, and the series is rapidly convergent beyond three–ion interactions. As in the corresponding theory of nontransition metals [3,5], the interatomic potentials are volume dependent but *structure independent* and thus rigorously transferable at a given volume to all bulk structures, either ordered or disordered. At constant volume Ω, the central–force pair potential v_2 is a one–dimensional function of the ion–ion separation distance $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$:

$$v_2(ij) \equiv v_2(R_{ij};\Omega) \,, \quad (2)$$

while the angular–force triplet potential v_3 and quadruplet potential v_4 are, respectively, the three– and six–dimensional functions

$$v_3(ijk) \equiv v_3(R_{ij},R_{jk},R_{ki};\Omega) \quad (3)$$

and

$$v_4(ijkl) \equiv v_4(R_{ij},R_{jk},R_{kl},R_{li},R_{ki},R_{lj};\Omega) \,. \quad (4)$$

In the full first–principles GPT, the potentials v_2, v_3, and v_4 are all nonanalytic functions with long–range oscillatory tails. For series–end transition metals (e.g., Cu), the multi–ion potentials can normally be neglected and applications performed using tabulated values of v_2. For the central transition metals (e.g., Mo), on the other hand, v_3 and v_4 are essential to a accurate description of materials properties. But unlike the simple radial function v_2,

Mat. Res. Soc. Symp. Proc. Vol. 193. ©1990 Materials Research Society

the multi–dimensional functions v_3 and v_4 cannot be readily tabulated and one is forced to recalculate these functions each time they are used. To improve this situation, a simplified model transition–metal GPT has been developed [6] in which v_3 and v_4 are approximated by analytic short–range forms that retain the dominant physics of the full first–principles theory. In all of the applications to Cu and Mo discussed below, we have utilized first–principles GPT potentials in the case of Cu and model GPT potentials based on scheme 1 of Ref. 6 in the case of Mo.

EXTENSION TO SURFACES

To deal with surfaces, one must make an internal transformation of the cohesive–energy functional (1) to an embedded–atom–like format [7,8] in which the atomic volume Ω is replaced by a suitable average electron density. The theory behind this transformation is discussed in Ref. 9. Briefly, for the leading volume term in Eq. (1), the effective replacement is just

$$E_{vol}(\Omega) \rightarrow \frac{1}{N}\sum_{i} E_{vol}(\bar{n}_i) , \qquad (5)$$

where $\bar{n}_i$ is the average electron density on the site i due to its surrounding environment. Thus one immediately identifies the volume term E_{vol} in the GPT as the embedding function F in the embedded–atom method (EAM). Figure 1 compares these two quantities as a function of relative electron density in the case of Cu. In the regime of interest for surface physics ($n/n_0 < 1$ in Fig. 1), the correspondence is seen to be very close indeed.

Similarly, for the interatomic potentials v_2, v_3, and v_4 one has the replacement

$$v_m(ij\ldots;\Omega) \rightarrow v_m(ij\ldots;\bar{n}_{ij\ldots}) , \qquad (6)$$

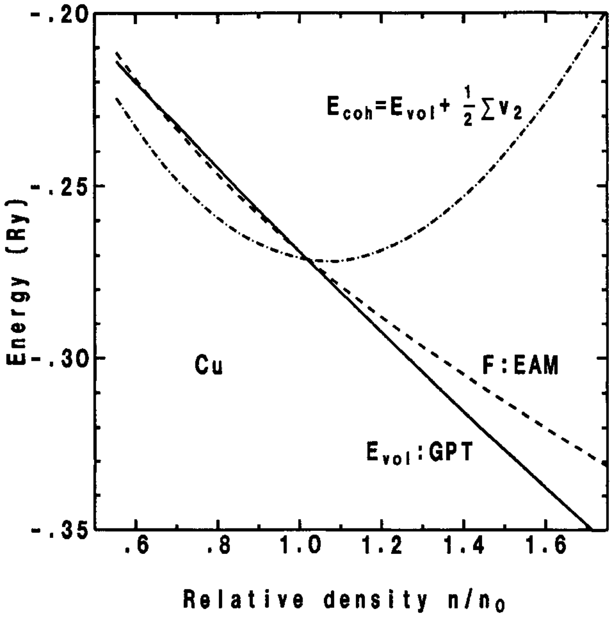

FIG. 1. Energy functionals for Cu: first–principles GPT volume term E_{vol} (solid line) and bulk cohesive energy E_{coh} (dot–dashed line); empirical EAM embedding function F from Ref. 8 (dashed line). The nonuniqueness of F has been dealt with here by adding a term linear in n/n_0 and imposing the normalization requirement that $F = E_{vol}$ at $n = n_0$, corresponding to the equilibrium bulk solid.