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## Structural phase transitions and specific-heat coefficients of alkaline-earth metals

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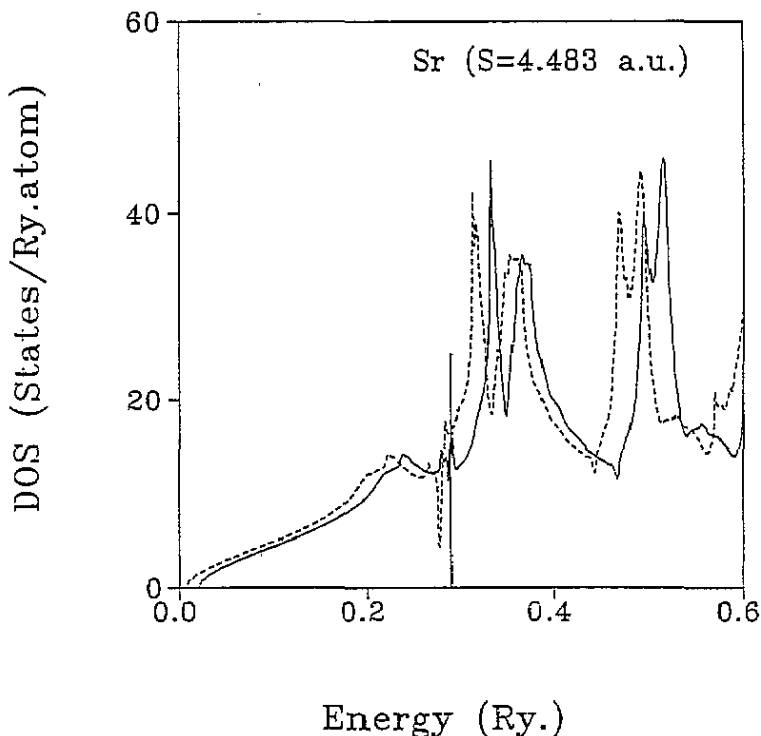
**Abstract.** The linear-muffin-tin-orbital method within the atomic-sphere approximation has been used to calculate the structural energy differences and specific-heat coefficients of the alkaline-earth metals. It has been shown that while non-local exchange corrections to the local-density approximation play almost no role for the structural energy differences, specific-heat coefficient values, especially for Sr, are correctly predicted only when these corrections are taken into account.

In recent years there has been a growing tendency to use the non-local exchange–correlation potentials [1, 2], as distinct from their local-density-approximation (LDA) analogues, in performing density-functional [3–5] calculations on solids. These calculations involve a large number of solids including transition, alkaline-earth and alkali metals. Since the reported data [6–8] on the alkaline-earth metals, especially for Sr, are fairly controversial, it is still a challenge to predict the stable crystal structures and specific-heat coefficients of these metals by use of local exchange–correlation potentials (ECPs) with and without including non-local corrections to the LDA.

For this purpose in the present work the linear-muffin-tin-orbital (LMTO) method [9] within the atomic-sphere approximation (ASA) is used for the local von Barth–Hedin (BH) [10] and Langreth–Perdew–Mehl (LPM) [11] ECP which includes such corrections. The calculations are performed by the codes given by Skriver [12] and the combined correction terms are included. The numbers of  $k$  points used in the irreducible portion of the Brillouin zone were 180, 240 and 285 for HCP, FCC and BCC structures, respectively. The self-consistency is achieved in such a way that the total energy value between the consecutive iterations was  $\pm 1 \times 10^{-6}$  Ryd. All the calculations are performed at the experimental Wigner–Seitz (WS) radii, which were computed from the experimental lattice constants [13] of the alkaline-earth metals. However, for Be, Mg and Ba, the total energies for different structures were compared at the same atomic volume, corresponding to the experimentally verified structure. This is reasonable since the total energy–volume curves for different structures of the same metal never intersect each other [14]. In the LMTO–ASA method the total energy of the solid was calculated in the frozen-core approximation, which proved to be convenient owing to problems associated with large core energies and the so-called double-counting terms [7, 12]. The results of the total-energy calculations are presented in table 1 for BH and LPM potentials. Table 1 clearly indicates that non-local exchange corrections to LDA are unimportant as far as the structural energy differences are concerned. This could be attributed to the fact that structural energy differences, when compared with those for alkali metals [14], are greater for alkaline-earth metals, yielding a suppression of

**Table 1.** Structural energy differences (in mRyd) of the alkaline-earth metals calculated at the experimental ws radii by use of BH and LPM exchange–correlation potentials. For Be and Mg,  $\Delta E = E_{\text{HCP}} - E_{\text{BCC}}$  whereas for Ca, Sr and Ba,  $\Delta E = E_{\text{FCC}} - E_{\text{BCC}}$ .

Crystal	$\Delta E$ (for BH)	$\Delta E$ (for LPM)	Low-temperature phase
Be	-6.476	-6.435	HCP
Mg	-0.809	-0.830	HCP
Ca	-0.835	-0.810	FCC
Sr	-1.824	-1.712	FCC
Ba	0.837	0.801	BCC



**Figure 1.** Total DOS curves for FCC Sr obtained by LPM (solid curve) and BH (dashed curve) exchange–correlation potentials at the experimental ws radius. The vertical line indicates the position of the Fermi level for the LPM curve at 0.29 Ryd. For the BH curve, the Fermi level is at the dip positioned at 0.28 Ryd.

the possible effects of these corrections. The structural ordering is in complete agreement with experimental observations [13].

However, for the electronic specific-heat coefficients there occur noticeably different values for BH and LPM potentials, as will be shown below. The electronic specific-heat coefficient  $\gamma$  is proportional to the total band-structure electronic density of states (DOS) at the Fermi energy [8]:

$$\gamma = 0.17335(1 + \lambda)N(E_F) \quad (1)$$

where the numerical constant is selected in such a way that the DOS at the Fermi level  $N(E_F)$  is given in states  $\text{Ryd}^{-1}/\text{atom}$  and  $\gamma$  is given in  $\text{mJ mol}^{-1} \text{K}^{-2}$ . In obtaining the  $\gamma$  values (table 2), in which the enhancement  $(1 + \lambda)$  due to electron–electron and electron–phonon interactions has not been included, after the last iteration of the self-consistency loop

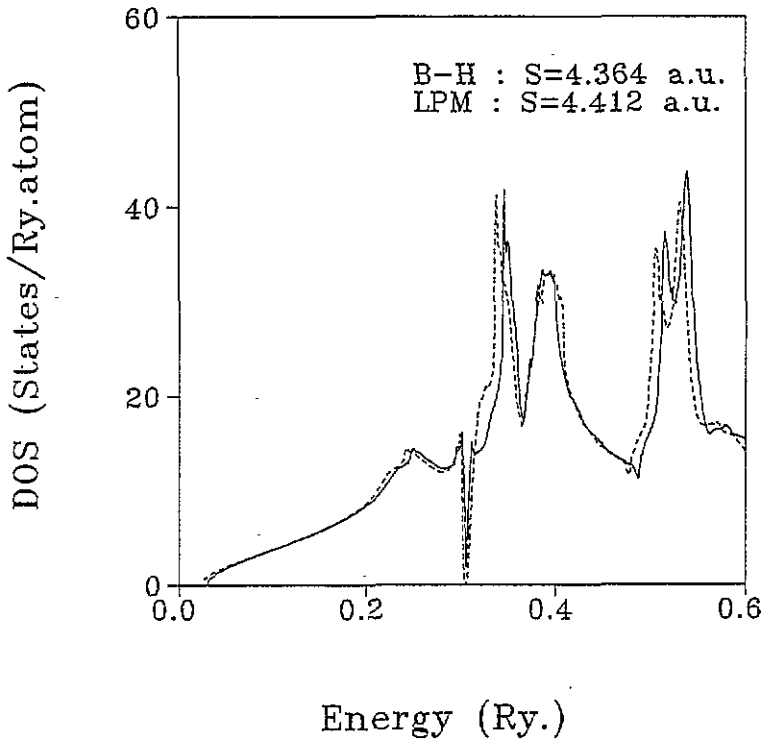


Figure 2. Total DOS curves for FCC Sr obtained by LPM (solid curve) and BH (dashed curve) exchange-correlation potentials at the theoretical  $w_s$  radii. The DOS at the Fermi level is 2.473 (states  $\text{Ryd}^{-1}/\text{atom}$ ) for the LPM and 0.0 (states  $\text{Ryd}^{-1}/\text{atom}$ ) for the BH curve.

Table 2. Calculated Fermi level quantities (in au) and the electronic specific-heat coefficients  $\gamma$  (in  $\text{mJ mol}^{-1} \text{K}^{-2}$ ) for BH and LPM exchange-correlation potentials (ECPs).  $\gamma_{\text{th}}$  is the APW result [8] and  $\gamma_{\text{exp}}$  is the experimental value [16].

Crystal	ECP	$E_F$	$N(E_F)$	$\gamma$	$\gamma_{\text{th}}$	$\gamma_{\text{exp}}$
HCP Be	BH	0.82	0.773	0.13	0.02	0.17
HCP Be	LPM	0.84	0.768	0.13		
HCP Mg	BH	0.44	4.759	0.82	1.03	1.30
HCP Mg	LPM	0.46	4.643	0.81		
FCC Ca	BH	0.30	19.125	3.32	2.97	2.90
FCC Ca	LPM	0.31	16.968	2.94		
FCC Sr	BH	0.28	3.460	0.60	0.00	3.60
FCC Sr	LPM	0.29	15.344	2.66		
BCC Ba	BH	0.27	14.125	2.45	2.69	2.70
BCC Ba	LPM	0.28	13.984	2.42		

was performed, the DDNS program [12], which calculates the total DOS and total number of states, was run only once in the vicinity of the Fermi level, thus assuring the accuracy of the calculated  $N(E_F)$  up to three digits. We have also applied the standard numerical techniques such as Neville's and Newton's interpolation formulae [15] in obtaining the  $N(E_F)$  values, yielding the similar results given in table 2.

According to table 2, use of the LPM potential yields consistent results with regard to experiment [16] when compared with the local BH potential or the APW predictions [8]. We should point out that the total DOS curves for alkaline-earth metals, except for Sr, are

similar to those presented in [8]. On the other hand, a serious discrepancy occurs for FCC Sr for local ECPs. In order to demonstrate this clearly, the total DOS curves for LPM and BH potentials are presented for Sr at the experimental WS radius  $S = 4.483$  au in figure 1. We should emphasize that the general appearance of the BH curve is similar to those obtained by other local ECPs such as those of Ceperley–Alder [17], Wigner [18] and Vosko–Wilk–Nusair [19]. It is known that non-local contributions to the LDA are more important in the valency states of atoms and solids rather than the inner shells [11] and, according to table 2, the alkaline-earth metals with two electrons outside a closed shell should be treated in the LPM scheme, which represents a substantial improvement over all local approximations. The dip at the Fermi level found for local ECPs reflects the neglect of non-local exchange corrections to the LDA for Sr, which has valency electrons far from the nucleus where the valency charge density is small and where the non-local exchange contribution is important [11].

It is well known that commonly the LDA underestimates the lattice constant [1, 2] and therefore it could be interesting to see the results for the theoretical volume for Sr. For this purpose the total energies were calculated self-consistently over 10 lattice parameters for FCC Sr. The total energy–volume curve is obtained by fitting the results to a cubic polynomial and the equilibrium  $S$  value is determined as (in au) 4.412 and 4.364 for LPM and BH potentials, respectively. Although the LPM result is closer to the experimental value, corresponding specific-heat coefficients calculated for these  $S$  values were found (figure 2) to be inconsistent with the experimental value (table 2). This supports the suggestion of Janak *et al* [6] that errors occur in the theoretical calculations for atoms with more than one electron outside a closed shell, and that the muffin-tin approximation and local ECP may involve errors when used for energy-band calculations for these metals.

## Acknowledgments

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