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2000 J. Phys.: Condens. Matter 12 5871

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## The susceptibility maximum of $\text{ZrZn}_2$ at high pressure

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Received 12 April 2000, in final form 30 May 2000

**Abstract.** The electronic structure of  $\text{ZrZn}_2$  is calculated by a self-consistent linear muffin-tin orbital method within the atomic sphere approximation. From fixed-spin-moment calculations the magnetic moment  $M$  is estimated as a function of magnetic field  $H$ . By fitting the calculated values of  $M(H)$  to the form  $H = aM + bM^3 + cM^5 + dM^7 + eM^9$ , the coefficients  $a, b, c, d, e$  are estimated as functions of the lattice constant. It is shown that the values of  $a$  and  $b$  are negative and positive, respectively, at the observed lattice constant at ambient pressure. With decreasing lattice constant the value of  $a$  changes its sign from negative to positive, which means that the ferromagnetic state is unstable. At a lattice constant a little smaller than the critical one, the value of  $b$  also changes its sign from positive to negative. These results, together with the other coefficients  $c-e$ , indicate a broad maximum in the temperature dependence of the susceptibility when the effect of spin fluctuations is taken into account. However, the absolute value of  $b$  is so small that the metamagnetic transition does not occur. It is shown that the anomalous temperature dependence of the susceptibility of  $\text{ZrZn}_2$  observed recently at high pressure is well described by the present calculations.

### 1. Introduction

It is well known that  $\text{ZrZn}_2$  with cubic Laves phase structure is a weak ferromagnet in an itinerant-electron system. The magnetic moment is about 0.1–0.2  $\mu_B$  per molecule at low temperature and the Curie temperature  $T_C$  is 20–30 K. The observed linear Arrott plots [1] of  $M^2$  against  $H/M$ , where  $M$  and  $H$  are the bulk moment and magnetic field, indicate that this compound is a typical example described by the Landau theory [2]. By means of polarized neutron scattering measurements, a large degree of delocalization of Zr spin density was observed in  $\text{ZrZn}_2$  [3]. The magnetization at low field varies as  $T^2$  and a strong field dependence of the magnetization was observed even at low temperature. The susceptibility above  $T_C$  obeys the Curie–Weiss law. These results are well described by the spin-fluctuation theory given by Moriya [4] and Lonzarich and Taillefer [5].

Recent experimental results, however, show that  $\text{ZrZn}_2$  and  $\text{MnSi}$  are not simple itinerant-electron magnets at high pressures where the magnetic phase transition takes place. As predicted by the spin-fluctuation theory [4, 5],  $T_C$  decreases as  $(p_C - p)^{3/4}$  with increasing  $p$ , where  $p_C$  is the critical pressure [6–8]. However, above  $p_C$  a maximum in the temperature dependence of the susceptibility was observed for  $\text{ZrZn}_2$  [6] and  $\text{MnSi}$  [7, 8]. No evidence for a first-order transition was observed for  $\text{ZrZn}_2$  near  $p_C$ . On the other hand, a clear metamagnetic transition (MT) from the paramagnetic to the magnetic (conical spin) state was observed for  $\text{MnSi}$  under high pressure [7–9]. The observed electric resistivities  $\rho$  for  $\text{ZrZn}_2$  and  $\text{MnSi}$  do

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not show a  $T^2$ -dependence but show a non-Fermi-liquid-like form  $\propto T^{1.6}$  associated with the quantum phase transition near  $p_C$  [6, 7, 10]. In fact, the self-consistently renormalized theory of spin fluctuations gives  $\rho \propto T^{5/3}$  near  $T_C$  [11].

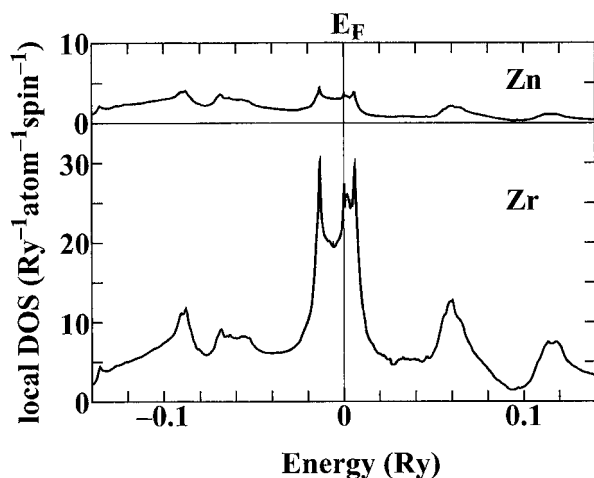
Yamada and Terao [12] have recently discussed the anomalous magnetic properties of MnSi at high pressure; they performed band-structure calculations for some lattice constants in a self-consistent linear muffin-tin orbital (LMTO) method within the atomic sphere approximation (ASA). They have found that the Landau coefficient  $a$  of  $M^2$  in the magnetic energy  $\Delta E(M)$  increases with increasing lattice constant and changes its sign from negative to positive. The coefficient  $b$  of  $M^4$  in  $\Delta E(M)$  is negative and large. They have shown that the MT may occur for MnSi at a lattice constant where the coefficient  $a$  is positive and small and  $b$  is negative. A susceptibility maximum was also explained by their calculated results when the effect of spin fluctuations was taken into account. This is just the itinerant-electron metamagnetism [13], similar to that observed for YCo<sub>2</sub> and Co(S, Se)<sub>2</sub> at ambient pressure [14, 15]. However, it is not clear why the MT occurs for MnSi but does not occur for ZrZn<sub>2</sub>.

In the present paper, similar calculations to those in [12] are carried out for ZrZn<sub>2</sub> to study the susceptibility-maximum phenomenon and the possibility of the MT. In section 2, the magnetic moment is obtained from a spin-polarized band calculation at various lattice constants. The pressure dependence of the magnetic moment is discussed. In section 3, fixed-spin-moment (FSM) calculations are carried out and the magnetization curve is obtained at various lattice constants. It is shown that there is no possibility of a MT for ZrZn<sub>2</sub> even at small lattice constants. Taking into account the effect of spin fluctuations, the susceptibility maximum observed for ZrZn<sub>2</sub> at high pressure is also discussed. Our conclusions and a discussion are given in section 4.

## 2. Calculation of the magnetic moment

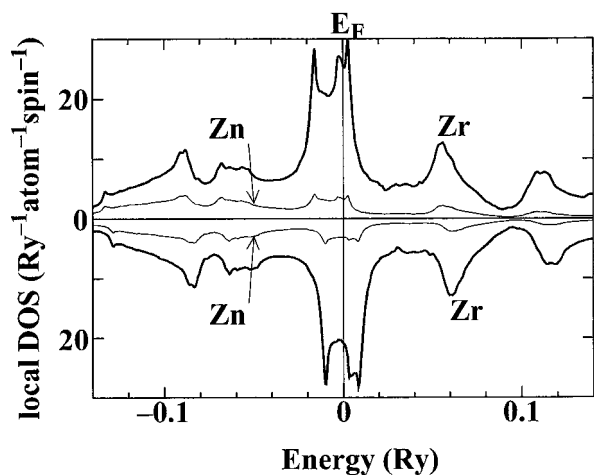
The electronic structure of ZrZn<sub>2</sub> with cubic Laves phase structure is calculated using a self-consistent LMTO-ASA based on the local density functional approximation with the exchange–correlation potential given by von Barth and Hedin [16]. The unit cell contains two Zr and four Zn atoms. The ratio between the radii of atomic spheres for Zr at 8a sites and Zn at 16d sites is chosen to be  $\sqrt{3}/2$ , which is the value determined from the radii of touching rigid spheres. Self-consistent calculations are carried out at 328  $k$ -points in the irreducible 1/48 Brillouin zone. Compared with the case for previous calculations for ZrZn<sub>2</sub> [17–19], the present number of sampling  $k$ -points is very large; thus a higher accuracy of numerical calculations is obtained. The basis set with angular momenta up to  $l = 3$  is adopted for both Zr and Zn atoms.

Figure 1 shows the calculated results for the local density-of-states (DOS) curves for Zr and Zn in the non-magnetic state at the observed lattice constant 7.40 Å at ambient pressure. The shape of the DOS and the position of the Fermi level  $E_F$  are very similar to those calculated previously [18, 19]. It is clearly seen that  $E_F$  lies at a shoulder of the sharp peak of the DOS. The dominant character near  $E_F$  is that of 4d states of Zr mixed mainly with 4p states of Zn. The height of the total DOS at  $E_F$ ,  $D(E_F)$ , is 69.0 states Ryd<sup>-1</sup>/molecule, which is almost the same as that calculated in [18, 19] and rather smaller than 220 states Ryd<sup>-1</sup>/molecule estimated from the observed low-temperature specific heat coefficient [20]. The difference between the calculated and observed values is attributable to the electron–phonon interaction and to the effect of spin fluctuations. The calculated value of  $D(E_F)$  is a little higher than that estimated from the Stoner criterion  $ID(E_F) > 1$ , where  $I$  is the exchange–correlation integral as discussed below.



**Figure 1.** Local DOS curves for Zr and Zn for paramagnetic  $ZrZn_2$  calculated at the observed lattice constant 7.40 Å.  $E_F$  denotes the Fermi level.

From spin-polarized band calculations, the ferromagnetic moment is obtained at lattice constants larger than 7.36 Å where the ferromagnetic state becomes stable. In figure 2 the local DOS curves of the majority- and minority-spin bands calculated at the lattice constant 7.46 Å are shown. In figure 3 the calculated magnetic moment  $M$  is plotted as a function of the lattice constant. An observed moment of about  $0.15 \mu_B/\text{molecule}$  is obtained at 7.44 Å, which is a little larger than the observed lattice constant 7.40 Å. The broken curve in figure 3 is plotted by assuming  $M \propto \sqrt{a - a_C}$  near  $a_C$ , where  $a$  is the lattice constant and  $a_C = 7.36$  Å. We can see a strong dependence of  $M$  on the lattice constant. A strong pressure dependence of the magnetic moment was actually observed in [21]. The value of  $d \ln M / d \ln V$  is estimated as 26.4 from figure 3 between 7.42 and 7.46 Å; this is rather large compared to those for other ferromagnetic materials—e.g.,  $d \ln M / d \ln V = 16$  for MnSi [9]. The value of  $d \ln M / dp$ , estimated by assuming the same value for the compressibility of  $ZrZn_2$  as that of MnSi, is  $1.9 \times 10^{-2} \text{ kbar}^{-1}$ , which is smaller than the observed one,  $4.4 \times 10^{-2} \text{ kbar}^{-1}$  [21]. It is noted that the observed magnetic moment and Curie temperature of  $ZrZn_2$  are very sensitive to impurities and stress. For instance, the observed value of  $p_C$  [21] is very different from that in [6, 22].



**Figure 2.** The local DOS of Zr and Zn for ferromagnetic  $ZrZn_2$  calculated at 7.46 Å.  $E_F$  denotes the Fermi level.

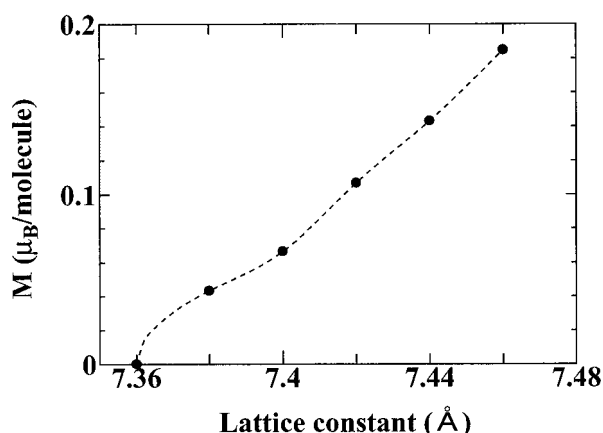


Figure 3. Calculated magnetic moments (closed circles) as functions of the lattice constant.

### 3. FSM calculations and the susceptibility maximum

The FSM calculations [23, 24] are carried out in the following way. The numbers of electrons with majority and minority spins,  $N_+$  and  $N_-$ , are given by  $(N+M)/2$  and  $(N-M)/2$  where  $N$  and  $M$  are the total number of valence electrons and the spin moment divided by  $\mu_B$ . Under the constraint of fixed values of  $N_+$  and  $N_-$ , the electron densities  $n_+(r)$ ,  $n_-(r)$  and the potentials for electrons can be calculated by using the usual Kohn–Sham self-consistent equations, which give two Fermi levels  $\mu_+$  and  $\mu_-$  in the majority- and minority-spin bands, respectively. For an arbitrary  $M$ , the system is not in the equilibrium state, so  $\mu_+ \neq \mu_-$ . However, the constrained state becomes an equilibrium at the magnetic field  $H = (\mu_+ - \mu_-)/2\mu_B$ , as  $\partial \Delta E(M)/\partial M = H$  and  $\partial \Delta E(M)/\partial N_{\pm} = \mu_{\pm}$ . This means that the state with the given  $M$  is stabilized at this  $H$ . That is,  $M$  is obtained as a function of  $H$ .

The closed and open circles in figure 4 denote  $\mu_+$  and  $\mu_-$ , respectively, calculated at the observed lattice constant 7.40 Å. The two curves for  $\mu_+$  and  $\mu_-$  intersect with each other at about  $M = 0.068 \mu_B$  per molecule. At this value of  $M$ , the value of  $H$  which stabilizes the state becomes zero. That is, the value of  $M$  gives the spontaneous spin moment. The spin moment calculated at the present lattice constant is about half of the observed value  $0.15 \mu_B$  per molecule [1]. As mentioned above, the observed value was obtained at a slightly larger lattice

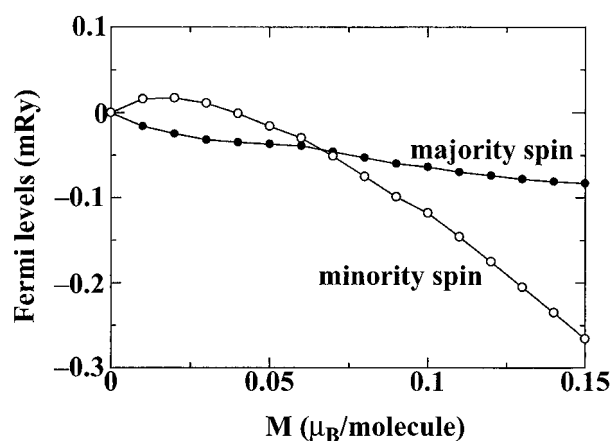


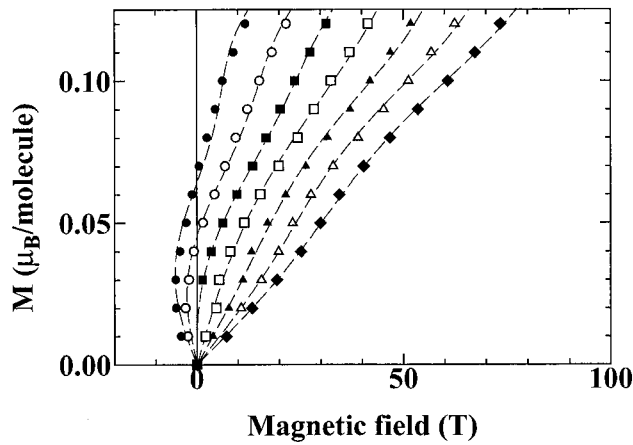
Figure 4. Fermi levels  $\mu_+$  (closed circles) and  $\mu_-$  (open circles) in the majority- and minority-spin bands, respectively, calculated at the observed lattice constant 7.40 Å.

constant of about 7.44 Å. Moroni *et al* [25] have performed fixed-spin-moment calculations for  $ZrZn_2$  at the lattice constants 7.62 and 7.30 Å. The total energy  $\Delta E(M)$  relative to the reference energy at  $M = 0$  was found to be very flat in the region of small  $M$ . Thus it was very hard to estimate an accurate value of  $M$  from the minimum of the calculated  $\Delta E(M)$ , even at the larger lattice constant 7.62 Å.

The symbols in figure 5 show the magnetization curves  $M(H)$  estimated at certain values of the lattice constant by using the calculated values of  $\mu_+$  and  $\mu_-$  and the relation  $H = (\mu_+ - \mu_-)/2\mu_B$ . By the least-mean-squares method, the calculated values of  $H/M$  as a function of  $M^2$  (Arrott plots) are fitted, in the range of  $M < 0.12 \mu_B/\text{molecule}$ , very well by the form

$$\frac{H}{M} = a + bM^2 + cM^4 + dM^6 + eM^8. \quad (1)$$

The thin broken curves in figure 5 are plotted by using these estimated values of the coefficients  $a, b, c, d$  and  $e$ . The region of negative fields has no physical meaning. Metamagnetic behaviour of  $M(H)$  cannot be seen for any lattice constant, although it can be seen that  $M(H)$  bends upward at smaller lattice constants.



**Figure 5.** Calculated magnetization curves at the lattice constants 7.40, 7.38, 7.36, 7.34, 7.32, 7.30 and 7.28 Å shown by closed and open circles, closed and open squares, closed and open triangles and closed diamonds, respectively. The thin broken curves are those calculated by using  $a$ - $e$  estimated in the text.

The estimated values of the coefficients  $a, b, c, d, e$  in (1) are plotted in figure 6 as functions of the lattice constant. It is found that the coefficient  $a$  increases with decreasing lattice constant and changes its sign from negative to positive at 7.36 Å, which indicates the collapse of the ferromagnetic state. As mentioned in section 1, such an instability of the ferromagnetic state was actually observed at the pressures 8 kbar [6, 22] and 18 kbar [21]. From the values of  $a$  and  $D(E_F)$  obtained at the observed lattice constant 7.40 Å, the Stoner factor  $S (=1 - I\chi_0)$  is estimated as  $-0.076$ , where  $\chi_0$  is the non-interacting susceptibility obtained from  $D(E_F)$ . Therefore, the Stoner condition  $S \leq 0$  for the appearance of the ferromagnetic moment is satisfied at this lattice constant. In figure 7, the calculated values of the total DOS  $D(E_F)$  at  $E_F$  and the Stoner factor  $S$  are plotted as functions of the lattice constant. On the other hand, the coefficient  $b$  decreases with decreasing lattice constant and changes its sign at about 7.33 Å. The other coefficients  $c, d$  and  $e$  also change their signs near these lattice constants.

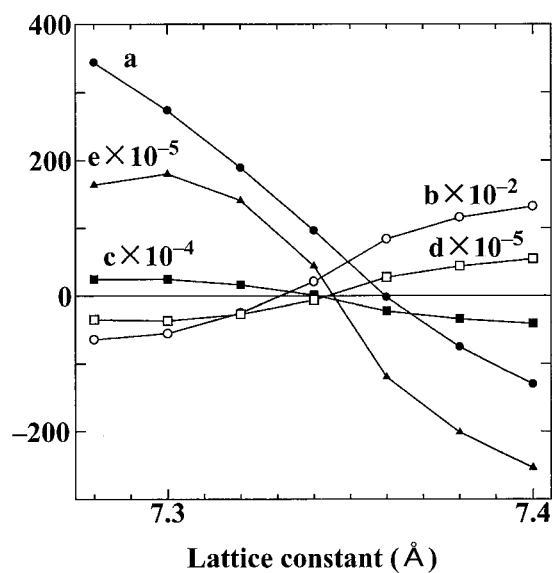


Figure 6. Estimated values of the coefficients  $a$  in  $T \mu_B^{-1}/\text{cell}$ ,  $b$  in  $T \mu_B^{-3}/\text{cell}^3$ ,  $c$  in  $T \mu_B^{-5}/\text{cell}^5$ ,  $d$  in  $T \mu_B^{-7}/\text{cell}^7$  and  $e$  in  $T \mu_B^{-9}/\text{cell}^9$ .

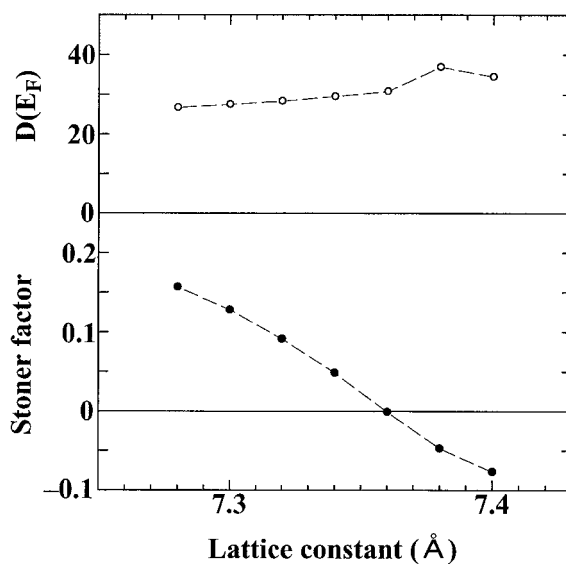


Figure 7. The total DOS  $D(E_F)$  at  $E_F$  in states  $\text{Ryd}^{-1}/(\text{molecule spin})$  and the Stoner factor  $S$  as functions of the lattice constant.

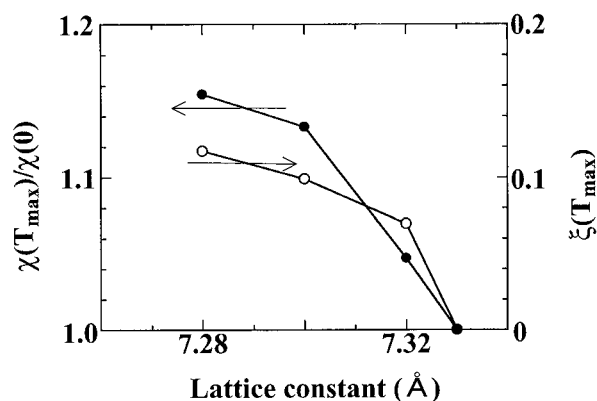
On taking into account the effect of spin fluctuations, the inverse of the spin susceptibility  $\chi(T)^{-1}$  is given by

$$\chi(T)^{-1} = a + \frac{5}{3}b\xi(T)^2 + \frac{35}{9}c\xi(T)^4 + \frac{35}{3}d\xi(T)^6 + \frac{385}{9}e\xi(T)^8 \quad (2)$$

where  $\xi(T)^2$  is the mean square amplitude of the spin fluctuations. Details of the derivation

of equation (2) are given in [12, 13]. Here, we assumed that the temperature dependence of  $\chi(T)$  comes from that of  $\xi(T)$  and that the coefficients  $a$ – $e$  in equation (1) do not depend on temperature. This is fairly reasonable because the main temperature dependence of  $\chi(T)$  comes from thermal spin fluctuations [4, 5].

When  $a > 0$  and  $b < 0$ , the susceptibility shows a maximum in its temperature dependence [13]. This is seen in the case for lattice constants smaller than 7.33 Å. The susceptibility maximum  $\chi(T_{\max})$  is obtained from  $\partial\chi(T)^{-1}/\partial\xi(T)^2 = 0$ , as  $\xi(T)^2$  is known to be a monotonically increasing function of temperature [4, 5]. The estimated values of  $\chi(T_{\max})/\chi(0)$  and  $\xi(T_{\max})$  are shown in figure 8. The observed values of  $\chi(T_{\max})/\chi(0)$  at high pressures are, in fact, smaller than 1.3 [6]. The observed value of  $T_{\max}$  seems to shift to high temperature with increasing pressure [6], which is consistent with the present calculations of  $\xi(T_{\max})$ .



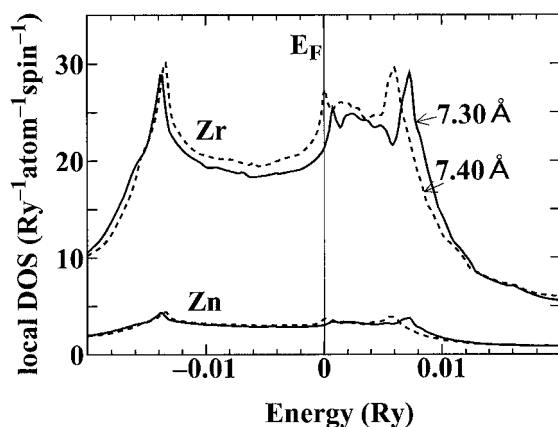
**Figure 8.** Calculated results for  $\chi(T_{\max})/\chi(0)$  (closed circles) and  $\xi(T_{\max})$  in  $\mu_B$ /molecule (open circles) as functions of the lattice constant.

#### 4. Conclusions and discussion

In the present paper, the electronic structures of  $ZrZn_2$  were calculated by using a self-consistent LMTO-ASA. From fixed-spin-moment calculations, the magnetic moment  $M$  is estimated as a function of magnetic field  $H$  for some lattice constants. From the calculated values of  $M(H)$ , the expansion coefficients  $a, b, c, d, e$  in equation (1) were estimated as functions of the lattice constant. It has been found that the values of  $a$  and  $b$  are negative and positive, respectively, at the observed lattice constant at ambient pressure. With decreasing lattice constant, the value of  $a$  changes its sign from negative to positive. At a lattice constant a little smaller than the critical one where  $a = 0$ , the value of  $b$  was also found to change its sign from positive to negative.

In order to see why the coefficients  $a$  and  $b$  change their signs with decreasing lattice constant, the local DOS curves near  $E_F$  in the non-magnetic state, calculated at the lattice constants 7.30 and 7.40 Å, are shown in figure 9. It is clearly seen that the sharp peak of the local DOS of Zr shifts toward the higher-energy side with decreasing lattice constant. The position of  $E_F$  moves out of the sharp peak of the DOS and comes into the region where  $a > 0$  and  $b < 0$ . It has been explicitly shown in this paper that these results, together with the other coefficients  $c$ – $e$ , indicate a broad maximum in the temperature dependence of the susceptibility at smaller lattice constants when the effect of spin fluctuations is taken into account. Moreover,





**Figure 9.** Local DOS curves in the non-magnetic state calculated at 7.30 and 7.40 Å, shown by solid and broken curves, respectively.  $E_F$  denotes the Fermi level.

it has been shown that the MT does not occur for  $ZrZn_2$  at any lattice constant, as the absolute value of  $b$  is so small. In this way the susceptibility maximum and the lack of evidence of the MT observed for  $ZrZn_2$  have been shown to be well explained by the present calculations.

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