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Compressibility and internal pressure anomalies of liquid 3d transition metals

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In honor of Martin Peter's 60th birthday.

Abstract. Some liquid 3d transition metals show anomalies in compressibility and atomic volume, just as they do in the solid phase. Compressibility data are analyzed in the hard-sphere model to find reduced package fractions and internal pressures for Cr, Mn, Fe, Co. A reference state can be defined and the excess quantities are interpreted as disordered local magnetic moments in a Stoner model.

1. Introduction

d-electrons confer to transition metals peculiar properties, e.g. strong cohesion, high melting points, high electrical resistivity etc. Indeed, the cohesive energies and bulk moduli show a regular variation peaking to a maximum for the refractory metals in the middle of the series (Friedel 1964). The trend is well apparent for the 2nd and 3rd series, however, in the 1st series deviations are due to what Friedel called 'magnetic complications' (Fig. 1 at left). Janak and Williams (1976) have attributed the anomalies in atomic volume and in bulk modulus for antiferromagnetic Cr, Mn and ferromagnetic Fe, Co, Ni to giant magnetic internal pressures.

At first thought, one would expect that 'magnetic complications' and structural effects are absent, or smeared out in cohesion properties of the liquid metals. The conjecture can be checked. Elastic properties and surface energies bear some relations for the solid and the liquid state (Frenkel 1942, Gilman 1960, Waseda and Jacob 1981). These relations indicate that the isothermal bulk modulus K_T of the liquid metal is approximately proportional to its surface tension γ , i.e. $\gamma/K_T \approx \text{const}$. Data on surface tension are plentiful (Fig. 1 at right) and in particular it is seen that liquid 3d transition metals behave different than the 4d and 5d metals. It is thus expected that, regarding $K_T \sim \gamma$, the bulk moduli of the liquid 3d transition metals show a same anomalous variation through the series as they do in the solid state. The 'magnetic complications' seem to persist in the liquid state. Grimvall (1976) is more explicit; from a analysis of the

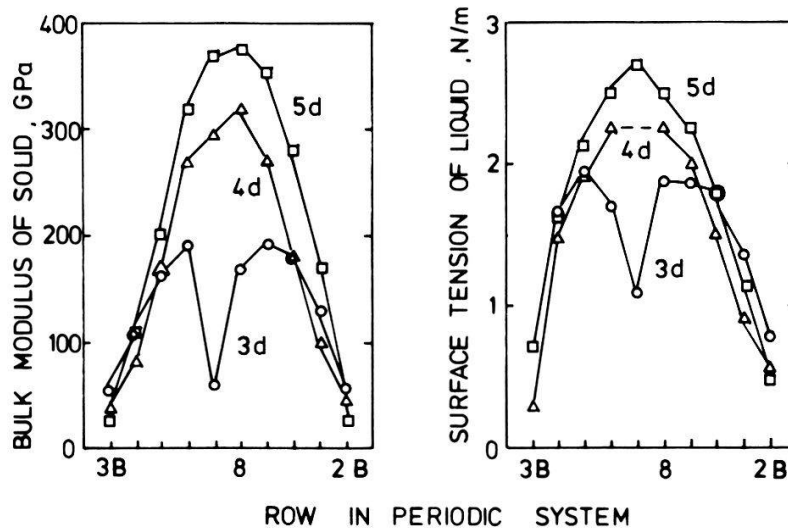


Figure 1

Bulk moduli of the solid (at left), and surface tension of the liquid (at right) 3d, 4d and 5d transition metals. Data from Gschneider (1964), Darling (1966) and Allen (1972).

temperature-pressure phase diagram of iron he draws the conclusion that in the paramagnetic solid and in the liquid state, this metal shows persistent but local spin split bands and disordered moments.

The bulk modulus is the quantity most sensitive to structural changes and pressure. Measurements for liquid Cu through Ti are analyzed and discussed from the viewpoint of atomic and magnetic structure.

2. Bulk moduli and atomic structure of 3d transition metals

Keita et al. (1981) and Casas et al. (1984) have measured the speed of sound v_s by aid of the variable-path method either in a crucible and buffer rods made of ceramics (Cu to Mn) or in the floating-zone of a metal bar (reactive Cr to Ti). The adiabatic bulk moduli are then calculated with $K_S = \rho v_s^2 = A v_s^2 / \Omega$. Some needed data and results are given in Table 1. The measured adiabatic bulk moduli

Table 1
Bulk moduli and hard-sphere parameters of liquid transition metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
T_m , °C	1538	1660	1890	1857	1244	1535	1495	1455	1083	419
Ω at m.p., cm ³ /mole [*])	15.4	11.6	9.48	8.27	9.55	7.94	7.61	7.48	7.95	9.95
K_S at m.p., GPa	—	80.4	121	116	34.3	108	126	128	94.4	53.4
$\gamma = c_p/c_v$ at m.p.	—	1.31	1.42	1.42	1.09	1.28	1.35	1.38	1.28	1.10
K_T at m.p., GPa	—	61.4	85.2	81.7	31.5	84.4	93.3	92.8	73.8	48.8
η	—	0.46	0.46	0.44	0.40	0.46	0.47	0.47	0.48	0.53
σ , nm	—	0.257	0.239	0.226	0.229	0.226	0.225	0.223	0.230	0.255

*) Data from Saito et al. (1969), Crawley (1974), CRC (1980).

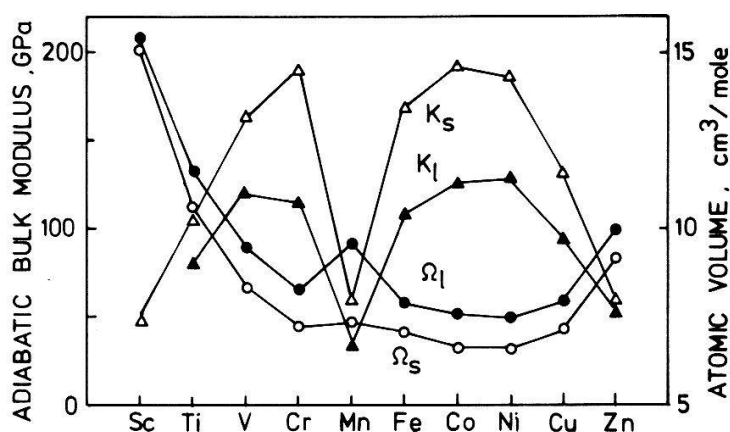


Figure 2
Bulk moduli and atomic volumes of the solid and liquid 3d transition metals.

are also shown in Fig. 2, together with the atomic volumes of the liquid and the same two properties for the solid state. It is seen that the trend through the series is the same for the solid and the liquid phases; liquid bulk moduli are reduced by about 30% from those of the solid state and atomic volumes of the liquid are 'blown-up' by about 12% respective to the solid phase.

Isothermal moduli can be obtained by the thermodynamic relation

$$\frac{K_S}{K_T} = \gamma = \frac{c_p}{c_v} = 1 + \frac{T\Omega\alpha^2 K_S}{Ac_p} \quad (1)$$

with A and Ω as atomic weight and atomic volume respectively. The specific heats c_p are known from different sources. Less is known for the coefficient of thermal expansion α ; in fact, it is wrong to identify the commonly measured temperature coefficient of mass density with $-\alpha$, because in a liquid the volume and coordination number change both with temperature (Ocken and Wagner 1966). Only measurements of the number densities $\rho_0 = \rho N_0/A$ are useful, as these are obtained with the gamma attenuation technique. Drotning (1981) has measured liquid Fe to Cu; $\alpha = -d \ln \rho_0/dT = (88-94) \cdot 10^{-6} \text{ K}^{-1}$, and varies few with the element. It is remarked that $d \ln \rho_0/dT \approx \frac{3}{4} d \ln \rho/dT$, thus giving quite different specific heat ratios. The γ 's thus obtained are listed in Table 1 and correspond to $c_v \approx 4R$. The result is reasonable and in fact theory gives 3R as ionic contribution and about 1R as electronic part (Yokoyama et al. 1983).

The isothermal bulk moduli derived from sound velocity measurements are shown in Fig. 3. In that same figure are given the results extracted from low- q structure factors measured by X-ray diffraction (Waseda and Ueno 1987). The two sets of data compare quite well.

It is established that the hard-sphere solution of the Percus-Yevich equation reproduces reasonably well the experimental structure factors of liquid normal, and transition metals (Waseda 1977, 1980). In this model, the compressibility equation connects the structure factor, or compressibility, to the packing fraction

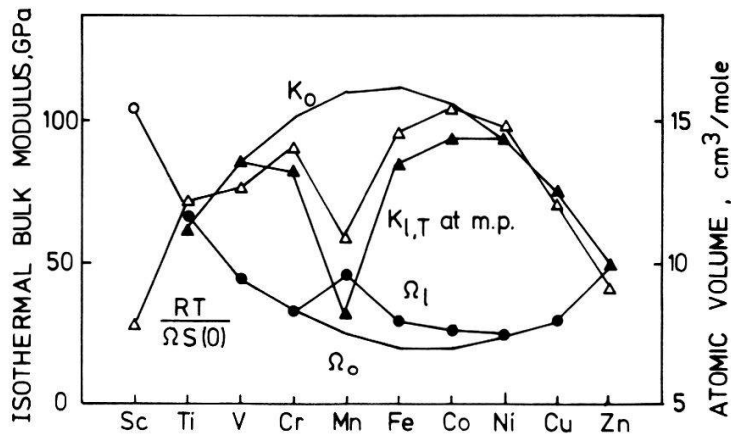


Figure 3

Isothermal bulk moduli (\blacktriangle from sound velocity, \triangle from low- q structure factors near the melting point (Waseda and Ueno (1987)) and atomic volumes of liquid 3d-transition metals. A parabolic fit for K and Ω over the 'anomalous' elements in the middle of the series is added.

η (Shimoji 1973)

$$\frac{RT}{\Omega} K_T^{-1} = S(q=0) = \frac{(1-\eta)^4}{(1+2\eta)^2}, \quad (2)$$

with

$$\eta = \frac{\pi N_0 \sigma^3}{6 \Omega}. \quad (3)$$

σ is the hard-sphere diameter. Using measured K 's, η and σ is calculated. It is seen in Fig. 4 that the packing fraction has low values for Cr, Mn, Fe, just as if the liquid would be 'blown up by an excess internal pressure'. On the other hand, the hard-sphere radii do not show a particular behaviour through the series. This must not be expected because, if the 'excess internal pressure' derives from a kinetic energy contribution, only the packing fraction is affected. Hard-sphere diameters and packing fractions derived from σ , as obtained from

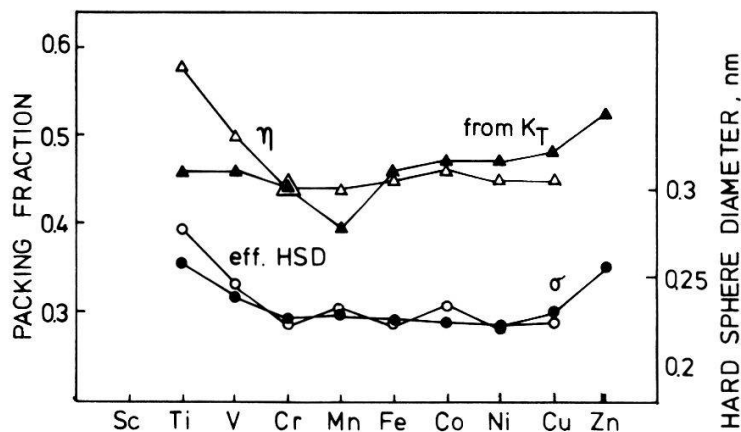


Figure 4

Packing fractions and hard-sphere diameters of liquid 3d transition metals (\blacktriangle , \bullet from bulk moduli using eqs. (2, 3); \triangle , \circ from structure factors (Waseda 1977, 1980)).

diffraction experiments (Waseda 1977, 1980), are also shown in Fig. 4; for these measurements, it is difficult to explain the large σ and η at the left of the series.

3. Internal pressure and magnetic structure

The bulk modulus is an equation of state related property, thus also the packing fraction. Anomalies in η , as depicted in Fig. 4, thus suggest to consider 'excess contributions' to the cohesion of the liquid.

From the equation of state for nonattracting rigid spheres by Carnahan and Starling (1969), the pressure is

$$\frac{P\Omega}{RT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad (4)$$

Results are shown in Fig. 5 and again, a strong deviation from a smooth parabolic variation through the series appears. It should be recalled that this pressure refers to kinetic energy, the only form of energy considered in the hard-sphere model of liquids.

Bulk moduli, atomic volume and internal pressure of liquid Cr, Mn, Fe, Co behave anomalous in the sense that they differ markedly from their 4d and 5d counterparts and from the behaviour in the remainder of the 3d series. For the solid state, a same trend is shown to be the mechanical implication of the kinetic energy increase due to magnetization (Janak and Williams 1976). Even above the Curie temperature (or Néel temperature), anomalies in cohesion properties persist and it is quite given to attribute these to the rather large disordered local moments, obtained by Heine et al. (1981), Pindor et al. (1983), and others. In fact, local moments suffice to induce a repulsion between the atoms and it does not matter if, on a larger scale, the moments are disordered instead of being in ferro- for antiferromagnetic alignment, because the repulsion is independent of

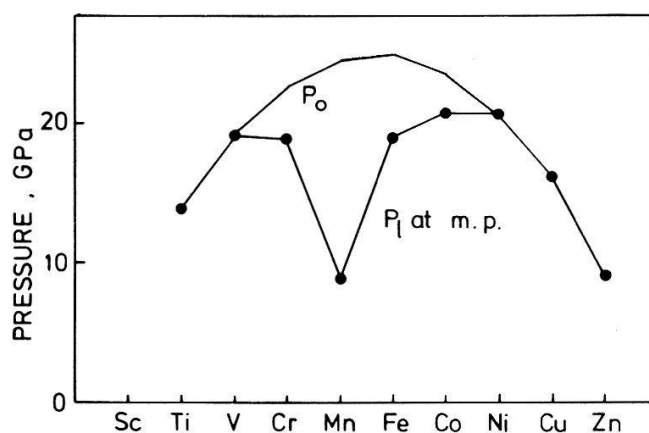


Figure 5

Internal pressure for liquid 3d transition metals. A parabolic fit over the 'anomalous' elements in the middle of the series is added.

the spin direction. This suggests to connect the anomalies in the liquid state equally well with the existence of disordered local moments.

The bulk moduli, atomic volumes and internal pressures in absence of magnetic interactions may be estimated using models for elastic constants of solid transition metals (Ducastelle 1970, Cyrot-Lackman 1980, Pettifor 1983). In these, the cohesive energy is approximated by the sum of a repulsive Born-Mayer contribution and a bond part depending explicitly on band filling n . It comes out that

$$K \sim U_{\text{coh}} \sim U_{\text{bond}} \sim n(10 - n) \quad \text{and} \quad \Omega \sim a(n - n_0)^2 + b, \quad (5)$$

i.e. both the bulk moduli and atomic volumes show a parabolic variation through the series. For solid metals it is $K \approx 3U_{\text{coh}}$ and for liquid 3d transition metals it is $K_S \approx 2.5 U_{\text{vap}}$. A same model is adopted as reference for the liquid metals and, by fitting a 2nd order polynomial on elements at the left (Ti, V) and at the right (Ni, Cu) of the series, the lines shown in Fig. 3 for K_0, Ω_0 are obtained. A same parabolic variation is expected for the internal pressure and traced in Fig. 5.

Following earlier arguments, the excess quantities $K_0 - K_l, \Omega_l - \Omega_0$ and $P_0 - P_l$ are considered as resulting from magnetic interactions. Pettifor (1980) suggests the amazingly simple picture of skewed partial densities of states as a model for the disordered local moment state. Scheme and phase diagram is shown in Fig. 6. The magnetic energy of the state is given by

$$U_{\text{dlm}} = -\frac{1}{20} (W_{\text{dlm}} - W)n(10 - n) + \frac{1}{4} Im^2 \quad (6)$$

with I as local spin density Stoner parameter; m is the moment of the local state. A broadened band has the width

$$W_{\text{dlm}} = \left[1 + 3 \left(\frac{\Delta}{W} \right)^2 \right]^{1/2} \cdot W, \quad (7)$$

where $\Delta = I \cdot m$ is the local splitting. This increase in bandwidth relates directly to the kinetic energy increase. It is straightforward to find the internal pressure

$$P_{\text{dlm}} = - \left(\frac{\partial U_{\text{dlm}}}{\partial \Omega} \right)_m = \frac{5}{3} \frac{W}{\Omega} \left[-\frac{1}{20} n(10 - n) + \frac{1}{6} \frac{W}{I} \right] \quad (8)$$

having used the scaling factor $d \ln W / d \ln \Omega = -5/3$ given by Heine (1967). Knowing $P_{\text{exc}} \equiv -P_{\text{dlm}}$, I/W may be extracted and used to calculate the magnetic moment

$$m^2 = \frac{1}{3} \left\{ \left[\frac{3}{10} n(10 - n) \right]^2 - \left(\frac{W}{I} \right)^2 \right\}. \quad (9)$$

For numerical values $W = 4.5$ eV (Khanna and Cyrot-Lackmann 1978) and $n = 4.6, 5.8, 7.0$ and 8.2 as number of d-electrons for Cr, Mn, Fe and Co respectively (Mott 1964) is used. Results are given in Table 2 and Fig. 6.

The disordered local moments in the liquids are smaller than those calculated

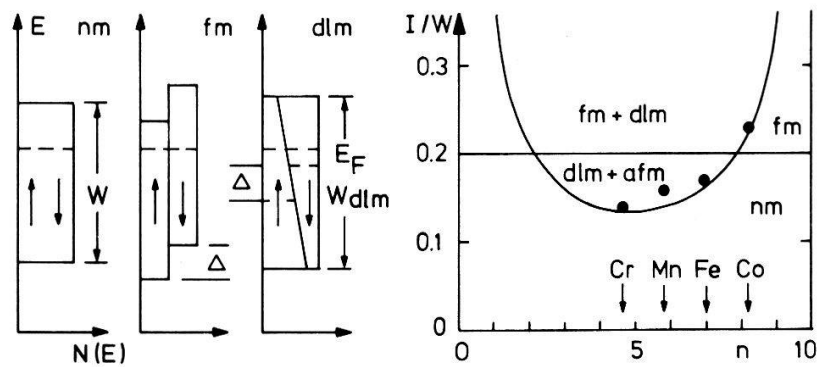


Figure 6
Band models for the nonmagnetic, ferromagnetic and disordered local moment states and the corresponding magnetic phase diagram. I/W values obtained for liquid metals are given.

for the solid metals and considerably reduced against the ferromagnetic state. The result for Cr seems uncertain; in fact, the specific heat ratio is rather large what results in small η , K_l and P_l values. It is more interesting to compare the internal magnetic pressures and the anomalies in compressibility. For Mn, Fe and Co, P_{dlm} in the liquid is about $\frac{1}{4}$ of P_{mag} in the solid. On the other hand, the relative reductions of the bulk moduli in the solid are about 0.27, 0.67, 0.45, 0.32 and 0.14 for Cr, Mn, Fe, Co and Ni respectively (taken from Janak and Williams 1976, Fig. 2) and are comparable in magnitude with those of the liquid (see Table 2, line 2). Thus, the magnetic pressure produces a same anomaly of compressibility in the solid and the liquid state, but it should be recalled that repulsive forces furnish the main contribution to K (DunCASTELLE 1970).

Table 2
Internal magnetic pressures, scaled Stoner parameters and magnetic moments.

	Cr	Mn	Fe	Co	Ni
$P_0 - P_l \equiv -P_{dlm}$, GPa	3.7	15.5	5.8	2.8	0
$(K_0 - K_l)/K_0$	0.19	0.71	0.24	0.12	—
$(\Omega_l - \Omega_0)/\Omega_0$	(-0.01)	0.22	0.13	0.09	—
I/W with $W = 4.5$ eV	0.14	0.16	0.17	0.23	
m , μ_B	1.1	2.1	1.3	0.5	
dlm in solid:					
m , μ_B ¹⁾	0	fcc 0 bcc 2.2	bcc 1.8 fcc 0.3	0	0
m at 1500 K, μ_B ²⁾			1.8	0.6	0
fm, afm in solid:					
m exp., μ_B	0.45	2.4	2.2	1.7	0.6
P_{mag} , GPa ³⁾	3.3	46	21	18	1.0

¹⁾ Heine et al. (1981)
²⁾ Pindor et al. (1983)
³⁾ Janak and Williams (1976)

4. Discussion

Evidence for persistent local moments in solid or liquid 3d transition metals is ordinarily derived from magnetic measurements or neutron scattering. In this work it is shown that all cohesion properties in the liquid state, i.e. compressibility, packing and internal pressure, are affected by magnetic interactions and that strong anomalies occur for chromium, manganese, iron and cobalt. Stoner theory is sufficient for their description and the local magnetic moments derive from itinerant electron states.

It might be objected that crude models have been used to analyze the atomic and magnetic structure of liquid transition metals. That might be true. However, to do this overview, analytical forms were needed and the hard-sphere model for atomic structure and skewed density of states model for magnetic structure are of this kind (see also the extensive discussion of models of magnetic metals by Heine et al. 1981). The main argument in this study, it should be recalled, is internal pressure and its anomalous variation through the series. Forces are required to account for anomalies in atomic volume and these are found to be very large.

In magnetic neutron scattering, Weber et al. (1978) find a pronounced small-angle scattering for molten iron and cobalt. The correlation length is 2.7 Å for Fe and 6.3 Å for Co, a dimension which is considerably larger than the hard-sphere diameters. The scattering is very weak for molten nickel and the estimated correlation length is only about 0.9 Å, thus less than the hard-sphere diameter. The results are explained by magnetic scattering from spin fluctuations. The anomalies in cohesion properties suggest to associate the small-angle scattering with plain local moments, however disorder (spin fluctuation do not produce a pressure). The authors also show the variations of the correlation length in terms of a reduced absolute temperature $(T - T_c)/T_c$ and that diagram lets expect that for molten Fe and Co, the correlation length falls below the hard-sphere diameters only for a multiple of the melting temperature. Then magnetic excitations (of Stoner type) should disappear.

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