

DIAMAGNETIC SUSCEPTIBILITY OF PURE METALS AND BINARY ALLOYS

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In order to facilitate the decomposition of experimental susceptibility data into its various contributions the diamagnetic susceptibility (χ_{dia}) of 31 metals with $Z \leq 49$ has been calculated from self-consistent charge densities. In dealing with binary alloys it is often assumed that χ_{dia} varies linearly with concentration between the values of the pure metals. Using selfconsistent charge densities for Cu–Rh it is shown that this assumption is valid in this alloy system.

1. Introduction

In discussing experimental susceptibility data it is often desirable or necessary to eliminate the diamagnetic susceptibility χ_{dia} in order to obtain information about the other contributions to the total susceptibility (e.g. refs. [1,2]). Because of the lack of calculations of χ_{dia} for metals various approximations for this part of the susceptibility, which are based on the assumption that only the tightly bound (ion core) electrons contribute to χ_{dia} , have been applied in the past. The approximations include the use of experimental magnetochemical diamagnetic susceptibilities of ions [3], or of theoretical diamagnetic susceptibilities for free atoms or ions, which are deduced from the results of either relativistic or nonrelativistic Hartree–Fock–Slater or Hartree–Fock calculations [4–6] using the equation:

$$\chi_{\text{dia}} = -\frac{e^2 N_A}{6mc^2} \sum_i \langle r_i^2 \rangle, \quad (1)$$

where the sum runs over the various atomic orbitals. Since the charge distribution in metals differs from that in free atoms or ions, these approximations cannot provide reliable values for

χ_{dia} of metals. Even if the charge density in metals is known it is not possible to calculate χ_{dia} by means of eq. (1) because it is not clear which electrons are to be considered as core electrons. These problems have been treated in a recent paper by Benkowitsch and Winter [7] who showed that all electrons within the Wigner–Seitz cell must be included in an expression for χ_{dia} analogous to that of eq. (1). Based on this result and using the charge distributions calculated by Moruzzi et al. [8] the diamagnetic susceptibilities of 31 metals have been calculated (section 2).

In binary alloys the concentration dependent diamagnetic susceptibility is often assumed to vary linearly between the values of the pure metals. By calculating the partial diamagnetic susceptibilities of Cu–Rh it is shown, that this assumption should in general be justified to a high degree of accuracy (section 3).

2. Diamagnetic susceptibility of metals

Recently Benkowitsch and Winter [7] developed a real-space method for the calculation of orbital susceptibilities of metals. This method im-

plies a partition of the total orbital susceptibility into three contributions. Two of them correspond to the conventional van Vleck and Landau contributions while the third one is analogous to the diamagnetic susceptibility of free atoms and ions (eq. (1)). For the longitudinal (z -)component of the diamagnetic susceptibility tensor they find:

$$\chi_{\text{dia}}^z = \frac{1}{\pi V_{\text{ws}}} \frac{e^2 N_{\text{A}}}{2mc^2} \int f(E) dE \times \int_{V_{\text{ws}}} d^3r \text{Im}[G^r(\mathbf{r}, \mathbf{r}, E)](x^2 + y^2), \quad (2)$$

where G^r is the retarded one-particle Green's function, \mathbf{r} is the position vector restricted to the Wigner-Seitz cell of volume V_{ws} and $f(E)$ is the Fermi distribution function. Note that χ_{dia} contains contributions from all electrons in the Wigner-Seitz cell because the energy integration extends over all occupied states. Obviously there is no restriction to core electrons as one could expect from eq. (1). In the case of cubic symmetry only the longitudinal component of the diamagnetic susceptibility remains. Using the total electron density $n(\mathbf{r})$ eq. (2) can therefore be simply expressed by:

$$\chi_{\text{dia}} = - \frac{e^2 N_{\text{A}}}{6mc^2} \int_{V_{\text{ws}}} n(\mathbf{r}) r^2 d^3r. \quad (3)$$

In the present work charge densities $\rho(\mathbf{r}) = en(\mathbf{r})$ given by Moruzzi et al. [8] have been used to calculate χ_{dia} for 31 pure metals with $Z \leq 49$ (table 1). These densities result from selfconsistent KKR-band structure calculations which were performed in a nonrelativistic manner and included exchange and correlation effects in the framework of local density theory. For metals possessing other than fcc or bcc structure the fcc structure was assumed by Moruzzi et al. (indicated by a "*" in table 1). For hcp metals this should affect χ_{dia} only slightly. Note that because the self-consistent potentials have been determined by minimizing the total energy, the theoretical lattice constants differ somewhat from the experimental ones. Compared with the result from section 3 for Cu which is based on the proper lattice constant this difference (about 1%) leads to an uncertainty for χ_{dia} of the same order of magnitude. As all metals

Table 1

Diamagnetic Susceptibilities of 31 Metals. (1) and (2): Element and atomic number; (3): Crystal structure of the metal. A "*" indicates that this structure is not the true one, but the structure assumed by Moruzzi et al. [8] in their calculation; (4): Diamagnetic susceptibility of the free ion (1+) [6]; (5): Diamagnetic susceptibility of the metal (present work); (6): Diamagnetic susceptibility of the free atom [5]. All susceptibilities are in $10^{-6} \text{ cm}^3/\text{mol}$. To obtain values in SI-units (m^3/mol) multiply by the factor $4\pi \times 10^{-6}$

(1)	(2)	(3)	(4)	(5)	(6)
Li	3	bcc	-0.7	-5.9	-14.8
Be	4	fcc*		-5.7	-13.7
Na	11	bcc	-4.8	-12.7	-21.5
Mg	12	fcc*		-14.8	-23.4
Al	13	fcc	-14.0	-15.8	-26.4
K	19	bcc	-14.3	-27.2	-40.3
Ca	20	fcc		-28.0	-44.5
Sc	21	fcc*		-25.3	-41.8
Ti	22	fcc*		-23.1	-39.4
V	23	bcc		-21.6	-37.3
Cr	24	bcc		-20.8	-31.3
Mn	25	fcc*		-20.3	-33.7
Fe	26	bcc		-19.8	-32.2
Co	27	fcc*		-19.4	-30.8
Ni	28	fcc		-19.3	-29.5
Cu	29	fcc	-14.4	-19.4	-25.1
Zn	30	fcc*	-18.2	-20.8	-27.2
Ga	31	fcc*	-19.3	-23.2	-31.9
Rb	37	bcc	-23.4	-39.0	-52.9
Sr	38	fcc		-40.3	-58.9
Y	39	fcc*		-37.6	-56.9
Zr	40	fcc*		-35.8	-54.6
Nb	41	bcc		-34.7	-47.9
Mo	42	bcc		-33.8	-46.1
Tc	43	fcc*		-33.4	-48.7
Ru	44	fcc*		-32.9	-42.9
Rh	45	fcc		-32.6	-41.5
Pd	46	fcc		-32.5	-34.0
Ag	47	fcc	-26.0	-33.0	-38.9
Cd	48	fcc*	-30.7	-35.2	-41.5
In	49	fcc*	-32.1	-38.2	-46.9

were assumed to have cubic structure χ_{dia} can be calculated from eq. (3). Because $\rho(\mathbf{r})$ has been treated in the muffin-tin approximation the integral in eq. (3) splits into two parts:

$$\chi_{\text{dia}} = - \frac{eN_{\text{A}}}{6mc^2} \times \left[4\pi \int_0^{r_{\text{MT}}} \rho(r) r^4 dr + \bar{\rho} \int_{V_{\text{WS}}} \int_{r > r_{\text{MT}}} r^2 d^3r \right], \quad (4)$$

where $\bar{\rho}$ is the averaged charge density outside the muffin-tin sphere of radius r_{MT} .

Choosing a set of suitable volume elements for the Wigner-Seitz cell (a rhombic dodecahedron for fcc and a truncated octahedron for bcc structure) the second integral is easily determined. Replacing the Wigner-Seitz cell by a sphere of the same volume would lead to only slightly smaller values for $|\chi_{\text{dia}}|$ (e.g., for Cu 1%).

3. Diamagnetic susceptibility of binary alloys

Because the diamagnetic susceptibility is expressed by means of the Green's function in eq. (2) this equation can be applied to the alloy problem by replacing $G^r(\mathbf{r}, \mathbf{r}, E)$ by the configuration averaged Green's function $\langle G^r(\mathbf{r}, \mathbf{r}, E) \rangle$. The partial diamagnetic susceptibilities $\chi_{\text{dia}}^A(c)$ and $\chi_{\text{dia}}^B(c)$ are then simply determined by the Green's functions projected onto the components or by the partial charge densities of the components respectively. The diamagnetic susceptibility is then given by:

$$\chi_{\text{dia}} = c\chi_{\text{dia}}^A(c) + (1-c)\chi_{\text{dia}}^B(c). \quad (5)$$

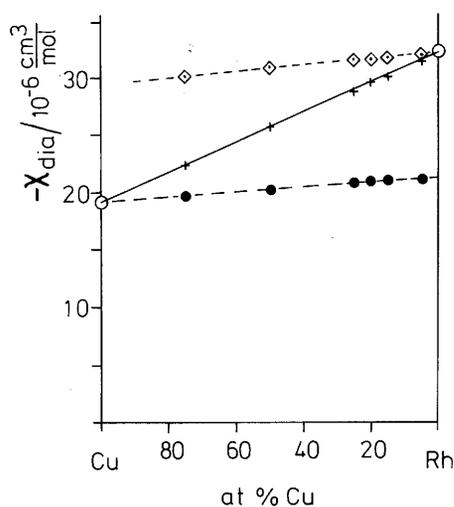


Fig. 1. Diamagnetic susceptibilities of CuRh Alloys. ●/◇ : partial diamagnetic susceptibilities of Cu/Rh; + : total diamagnetic susceptibility of CuRh; ○ : diamagnetic susceptibility of Cu and Rh from table 1. The straight line joins the values of the pure metals.

In general, the partial diamagnetic susceptibilities vary with concentration c and the total is not necessarily a linear function of c . Fig. 1 shows the partial and the total susceptibilities of Cu-Rh alloys based on charge densities provided by a self-consistent KKR-CPA band structure calculation [9]. The partial charge density of each component was used to calculate the partial diamagnetic susceptibilities at various concentrations in the same way as for pure metals and the total diamagnetic susceptibility then emerged from eq. (5).

4. Discussion

Pure metals

For comparison with our results the theoretical free atom and free ion susceptibilities [5,6] have been added to table 1. As can be seen, for all elements the metal value of the diamagnetic susceptibility lies between the free atom and the free ion value. For some elements the metal and the free ion values differ less than 12.5% (e.g., Al, Zn and Cd), so that for these elements the use of ionic values instead of metal values leads to acceptable but only rough approximations whereas for other elements neither the free ion nor the free atom values are reasonable as a substitute for the metal values.

The fact that for certain elements the diamagnetic susceptibilities of the metal and the free ion are nearly equal can be explained as a compensation of two effects: Going from a free atom to an atom in a crystal lattice results in a compression of the outer electron shells and therefore a reduction of the expectation values of r^2 . Going from the free atom to the free ion mainly results in a reduction of the sum of the $\langle r^2 \rangle$ because one electron less is included in the sum. For some elements these two effects nearly compensate and lead to the observed similar values for the metal and free ion diamagnetic susceptibilities.

Cu-Rh alloys

The partial diamagnetic susceptibilities of Cu and Rh in Cu-Rh and the total diamagnetic susceptibility of Cu-Rh are shown in fig. 1. The Cu

and Rh values were taken from table 1 and joined by a straight line.

The partial diamagnetic susceptibilities of both components show a weak but nevertheless visible concentration dependence which is mainly due to the increase of the lattice constant going from Cu to Rh.

Since the concentration dependence of both partial susceptibilities is nearly linear, the total diamagnetic susceptibility is also linear. Thus, although the partial diamagnetic susceptibilities vary with composition the total diamagnetic susceptibility can be approximated by a linear interpolation between the values for the pure components. This should also hold for other alloy systems where charge transfer effects are not too serious. For this reason estimations based on the values of table 1 should in general lead to good approximations for the total diamagnetic susceptibility of binary alloys.

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