Magnetic Susceptibility of the Cluster Compounds Mo_6Se_8 and Mo_6Te_8

G. Concas, F. Congiu, A. Geddo Lehmann, C. Muntoni, S. Sanna, and G. Spano

Dipartimento di Fisica, Universitá di Cagliari, and Istituto Nazionale per la Fisica della Materia,
S.P. Monserrato-Sestu Km 0.700, I-09042 Monserrato (Cagliari), Italy

Reprint requests to Dr. G. C.; Fax: +39 070 510171; E-mail: giorgio.concas@dsf.unica.it

The magnetic susceptibility of the cluster compounds Mo_6Se_8 and Mo_6Te_8 has been measured at temperatures between 82 and 330 K, using a Faraday balance. The paramagnetic and diamagnetic components of the susceptibility have been analyzed. The Pauli component was evaluated using the density of states at the Fermi level obtained by band structure calculations, while the core component was evaluated using the calculated atomic core diamagnetism. The paramagnetic susceptibility of Mo_6Se_8 is due mainly to the Pauli contribution, while the Van Vleck contribution is small, in agreement with the metallic feature of the compound. The paramagnetic susceptibility of Mo_6Te_8 is due mainly to the Van Vleck term, while the Pauli contribution of the conduction electrons is very small. The result points out that the Mo_6 clusters in the telluride retain their molecular character, with small intercluster interactions.

Key words: Chalcogenides; Molybdenum; Magnetic Susceptibility; X-ray Diffraction;
Chevrel Phases.

1. Introduction

The ternary molybdenum chalcogenides known as Chevrel phases are a class of compounds extensively studied in the 1970es for their superconducting properties [1] and more recently as candidates for new thermoelectric materials [2, 3]. Their general formula is $M_xMo_6X_8$, in which X = S, Se or Te and M can be a simple or transition metal atom, or a rare-earth element [4]. The building blocks of the crystal structure are binary Mo_6X_8 clusters, in which an octahedron of Mo atoms stays in a cubic X_8 cage formed by eight chalcogens. The three dimensional stacking of such clusters has overall rhombohedral symmetry, with Mo_6X_8 blocks twisted around the ternary axis, and contains large voids which can be filled with M metals to give ternary phases. Since the milestone paper of Andersen, Klose, and Nohl of 1978 [5] it was recognized that bonding in filled and unfilled Chevrel phases is mainly due to Mo and X atoms, with important Mo d - Mo d intracluster interactions and Mo d - X p covalent mixing. Successive studies agree on the basic feature of the overall distribution of the energy levels, i. e. a rough separation of the chalcogen p and Mo d states below the Fermi level, and the existence of a forbidden gap separating 12 Mo 4d states from the remaining 18 Mo 4d states [3, 6]. The Fermi level is just below this gap and lies in very narrow Mo 4d sub-bands which derive from the molecular orbital states of the isolated Mo_6 octahedra. In ternary phases, the metallic species M remains weakly coupled to the rest of the structure, with only secondary effects on the electronic properties, modifying the distance between the Mo_6X_8 clusters, and therefore Mo 4d bandwidth, and providing electrons for band filling. This implies important consequence on the physical properties. For instance, the phases based on rare-earth (RE) $REMo_6S_8$ and $REMo_6Se_8$ show coexistence of magnetic order and superconductivity [7]. This is possible because the crystal structure is formed by the two nearly-independent sublattices, the first one, made of the Mo_6X_8 units, which determines the transport and superconducting properties; the second one, made of the rare-earth atoms, which sustains the long range magnetic order.

The binary Chevrel phases Mo_6X_8, in which the metal voids are empty, permit the investigation of the properties of the cluster lattice alone. The aim of this work is to investigate the magnetic susceptibility of the binary Chevrel phases Mo_6Se_8 and Mo_6Te_8.

Table 1. X-Ray diffraction data for Mo_6Se_8. Relative intensities refer to peak heights. *hkl* are the rhombohedral Miller indexes and d_{exp} and d_{calc} are the experimental and calculated interplanar distances. Errors on the last digit are given in parentheses.

Intensity %	h	k	l	d_{exp} Å	d_{calc} Å
100	1	0	0	6.64(2)	6.652
21	2	0	0	3.330(6)	3.326
16	2	0	−1	3.016(5)	3.013
24	2	1	0	2.938(5)	2.938
23	2	−1	−1	2.765(4)	2.760
45	2	1	−1	2.732(4)	2.730
14	2	1	1	2.650(4)	2.647
9	2	0	−2	2.394(3)	2.390
5	2	2	0	2.316(3)	2.316
43	2	1	−2	2.250(3)	2.249
12	3	0	0	2.218(3)	2.218
19	2	2	1	2.157(2)	2.158
22	3	0	−1	2.126(2)	2.124
11	3	1	0	2.084(2)	2.084
80	3	1	−1	2.011(2)	2.012
9	3	0	−2	1.874(2)	1.872
15	2	2	2	1.862(2)	1.863
21	3	−1	−2	1.800(2)	1.807

Table 2. X-Ray diffraction data for Mo_6Te_8. Relative intensities refer to peak heights. *hkl* are the rhombohedral Miller indexes and d_{exp} and d_{calc} are the experimental and calculated interplanar distances. Errors on the last digit are given in parentheses.

Intensity %	h	k	l	d_{exp} Å	d_{calc} Å
71	1	0	0	7.01(3)	7.043
37	2	0	0	3.524(7)	3.522
12	2	0	−1	3.212(6)	3.210
62	2	1	0	3.092(5)	3.093
79	2	−1	−1	2.943(5)	2.944
36	2	1	−1	2.901(5)	2.900
11	2	1	1	2.769(4)	2.770
10	2	0	−2	2.548(4)	2.550
6	2	2	0	2.434(3)	2.434
42	2	1	−2	2.400(3)	2.400
8	3	0	0	2.348(3)	2.348
34	3	0	−1	2.258(3)	2.259
14	3	1	0	2.195(3)	2.197
100	3	1	−1	2.133(2)	2.132
4	3	1	1	2.064(2)	2.064
14	3	0	−2	1.997(2)	1.997
14	2	2	2	1.946(2)	1.945
44	3	1	−2	1.915(2)	1.914

2. Experimental Procedure

The compounds Mo_6Se_8 and Mo_6Te_8 can be synthesised by direct combination of the elements. Mo_6Se_8 has been prepared using high purity powders of molybdenum reduced in H_2 at 800 °C, and grains of selenium. Stoichiometric amounts have been mechanically homogenised and pressed in a hydraulic press. The *tablet* has been sealed under vacuum in a silica tube and heated at 800 °C for 2 days, 1000 °C for 2 days and 1150 °C for 2 days. The product showed traces of $MoSe_2$ in the X-ray diffraction (XRD) spectrum. Therefore a 2nd thermal treatment has been applied, at 1000 °C for 1.5 days and at 1200 °C for 3.5 days, after which the final product appeared homogeneous.

Mo_6Te_8 has been prepared using powders of molybdenum, reduced in H_2 at 800 °C, and pieces of tellurium. Stoichiometric amounts have been sealed under vacuum in a silica tube; heated at 950 °C for 11 days and on 1050 °C for 5 days. The final product was homogeneous at X-ray diffractometric analysis; in particular no peak of metallic molybdenum appeared in the spectrum.

The X-ray diffraction spectra were collected, using a θ - 2θ conventional powder diffractometer (Siemens D500) and Cu-K_α radiation.

The static magnetic susceptibility has been measured with the Faraday method using an RG Cahn electrobalance. The measurements have been performed on powder samples (150 mg) at temperatures ranging from 82 K to 330 K, with five different maximum magnetic fields, ranging from 0.63 T to 1 T. The susceptibility was found to be independent on the magnetic field, which rules out the presence of ferromagnetic impurities. The measurements at different temperatures have been performed under helium, using liquid air as cryogenic liquid. The measured susceptibilities were corrected for the diamagnetism of the sample holder.

3. Results

Table 1 and Table 2 give the XRD peaks of Mo_6Se_8 and Mo_6Te_8, indexed in the rhombohedral system. The lattice constants have been refined, using the peak positions, by means of a least squares routine. The rhombohedral parameters for Mo_6Se_8 are $a_r = (0.666 \pm 0.001)$ nm and $\alpha_r = (91.7 \pm 0.1)$ degrees, while Mo_6Te_8 has $a_r = (0.706 \pm 0.001)$ nm and $\alpha_r = (92.5 \pm 0.01)$ degrees. These values agree well with those reported in the literature [8].

Figure 1 shows the magnetic susceptibility of Mo_6Se_8 versus temperature, measured between 82 K
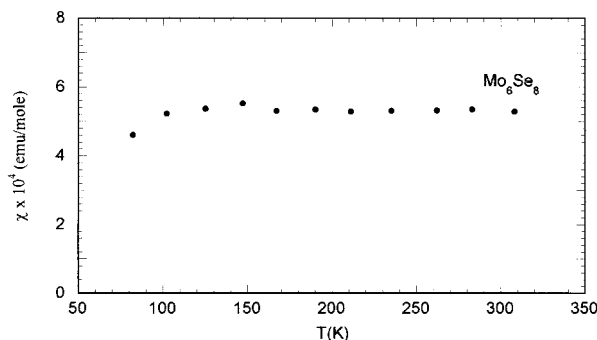
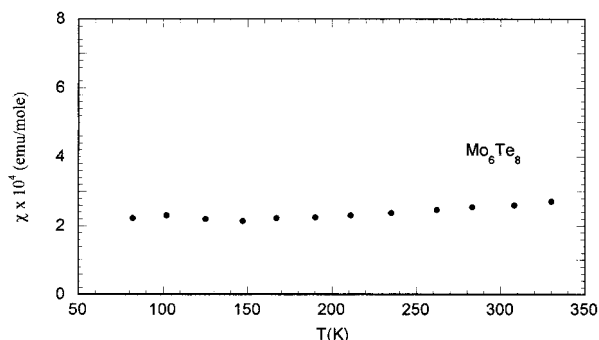Fig. 1. Magnetic susceptibility of Mo_6Se_8 between 82 and 308 K versus temperature.

Fig. 2. Magnetic susceptibility of Mo_6Te_8 between 82 and 330 K versus temperature.

and 308 K, corrected for a small Curie-like term due to paramagnetic impurities. The corrected susceptibility shows only a small dependence on temperature near 82 K. The value at room temperature (298 K) is $(5.28 \pm 0.10) \cdot 10^{-4}$ emu/mole.

Figure 2 shows the magnetic susceptibility of Mo_6Te_8 as a function of temperature, measured between 82 K and 330 K. It is only weakly temperature-dependent. The value of the susceptibility at room temperature (297 K) is $(2.59 \pm 0.03) \cdot 10^{-4}$ emu/mole.

4. Discussion and Conclusions

In the absence of paramagnetic Curie-like terms, the main contributions to the total magnetic susceptibility χ_{tot} in a solid are given by

$$\chi_{tot} = \chi_{core} + \chi_P + \chi_L + \chi_{VV},$$

where χ_{core} is the diamagnetic core component, χ_P and χ_L are the Pauli and Landau-Peierls spin susceptibilities of conduction electrons, and χ_{VV} indicates the orbital contribution to the paramagnetic susceptibility, analogous to the temuperature-independent Van Vleck paramagnetism of ions in crystal fields.

To separate the various terms appearing in the total susceptibility, we can first of all estimate the expected core diamagnetism, which can be evaluated using the calculated atomic diamagnetism of Mo^{+6}, Se^{-2} and Te^{-2} ions [9]. The core diamagnetic susceptibility has the value of $-4.26 \cdot 10^{-4}$ emu/mole for Mo_6Se_8 and of $-6.02 \cdot 10^{-4}$ emu/mole for Mo_6Te_8.

Among the spin terms, in the case of d electrons, treated in the tight binding approximation, the

Pauli component χ_P is of prime importance [10]. The Landau-Peierls diamagnetic susceptibility χ_L, which is proportional to m_e/m^* and that is equal to $-^1/_3\chi_P$ in the case of free electrons [11], can be safely neglected in the present case, owing to the low dispersion of the Mo 4d bands [10].

The Pauli component χ_P can be estimated from the value of the density of states at the Fermi level $D(E_F)$ by means of the relation

$$\chi_P = \mu_B^2 N D_\chi(E_F), \tag{1}$$

where μ_B is the Bohr magneton and N the Avogadro number.

The density of states $D_\chi(E_F)$ appearing in the previous expression is enhanced with respect to the band value $D(E_F)$ by the elec_tron-elec_tron interaction through the relation

$$D(E_F) = D_\chi(E_F)/(1 + I_{exch}D_\chi(E_F)), \tag{2}$$

in which I_{exch} is the electron-electron exchange interaction parameter [12].

The expected Pauli contribution to the measured susceptibility of Mo_6Se_8 and Mo_6Te_8 can be evaluated from (1) and (2), in which it is reasonable to use for I_{exch} the value obtained for metallic molybdenum ($I_{exch} = 0.04$ Ry) [5], owing to the fact that the exchange interaction is essentially intra-atomic and that, at E_F, the electronic states for Mo_6X_8 compounds have essentially Mo character. With the theoretical $D(E_F)$ of 12.83 states/(spin Mo-atom Ry) [13], we obtain $\chi_P = 7.75 \cdot 10^{-4}$ emu/mole for Mo_6Se_8. If we follow the same procedure for Mo_6Te_8, using a value of $D(E_F)$ of 0.5 states/(spin Mo-atom Ry) [13], we obtain $\chi_P = 0.15 \cdot 10^{-4}$ emu/mole, which is one

order of magnitude smaller than the measured susceptibility.

By subtracting the estimated χ_{core} and χ_P from the experimental susceptibility at room temperature, we obtain a residual paramagnetic susceptibility of $1.80 \cdot 10^{-4}$ emu/mole for Mo_6Se_8 and of $8.46 \cdot 10^{-4}$ emu/mole for Mo_6Te_8, indicating that in the selenide the Pauli component is the major term, while in the telluride the orbital paramagnetic contribution χ_{VV} is dominant. The previous results reflect the differences in the electronic properties of the two cluster compounds. Mo_6Se_8 is a metal and superconductor at $T_c = 6.7$ K, while Mo_6Te_8 is a semimetal and not superconductor. In Mo_6Se_8 the Fermi level falls in a peak of the density of states, resulting in a very high $D(E_F)$ with consequent relatively high critical temperature of superconductivity T_c and high spin paramagnetism above T_c, while E_F lies near a valley of the density of states in Mo_6Te_8 [5, 6, 13]. This difference can be understood on the basis of an ionic-covalent model for bonding in Mo_6X_8 clusters, which assumes that there are covalent interactions between Mo atoms and the chalcogens leading to an increase of the formal electric charge on the Mo_6 octahedron [14]. More specifically, only for X = S a formal valence of –2 can be assumed for the chalcogen [15], so that the eight sulphur atoms take 16 electrons from the six molybdenum atoms, and 20 electrons per Mo_6 unit remain in the Mo d bands (valence electron concentration VEC = 20). In the case of Se and Te, the formal valences are reduced to –1.8 and –1.7, respectively [15], leading to 21.60 d electrons for Mo_6Se_8 and of 22.4 d electrons for Mo_6Te_8. The lower 12 Mo d sub-bands are therefore differently filled in the three Mo_6X_8 clusters, a fact which shifts the position of the Fermi level within the bands.

A great deal of information about the band structure would be required to calculate and discuss the paramagnetic term χ_{VV}, the expression of which in the tight binding approximation may be written as [10, 11]

$$\chi_{VV} = \int \frac{d\mathbf{k}}{(2\pi)^3} \sum_{nn'} \frac{f(E_{nk}) - f(E_{n'\mathbf{k}})}{E_{n'k} - (E_{n\mathbf{k}}} \qquad (3)$$

$$\cdot \mu_B^2 \langle n\mathbf{k}|L|n'\mathbf{k}\rangle \langle n'\mathbf{k}|L|n\mathbf{k}\rangle,$$

in which $f(E_{nk})$ and $f(E'_{nk})$ are the Fermi functions for electrons in state $n\mathbf{k}$ and $n'\mathbf{k}$ with energies $E_{n\mathbf{k}}$ and $E_{n'\mathbf{k}}$, respectively, and L is the orbital angular momentum operator. The quantitative evaluation of the orbital paramagnetism in binary Mo_6Se_8 and Mo_6Te_8 clusters is beyond the aim of this work. However, among the few attempts which have been made at correlate expression (3) to a limited number of crucial band and bonding parameters, we would like to mention the one connecting χ_{VV} and bond character in complex diamond-like semiconductors [16, 17]. In that case the orbital paramagnetism is expressed as $\chi_{VV}^0(1 - \lambda)$, in which the covalency parameter $(1 - \lambda)$ varies in the range 1 to 0 from ionic to covalent compounds, and χ_{VV}^0 is the paramagnetic susceptibility in the case of purely exchange interactions. Following the idea of Pauling [18], the degree of ionicity of a bond, denoted by λ, can be related to the electronegativity difference Δx between the interacting atoms. For Mo-Se and Mo-Te bonds one has $\Delta x^{Se} = (2.4 - 1.8) = 0.6$ and $\Delta x^{Te} = (2.1 - 1.8) = 0.3$, so that an increase of χ_{VV} can be expected from Mo_6Se_8 to Mo_6Te_8, because the ionicity of the Mo-X bond decreases as one goes from the selenide to the telluride. It can be speculated that in the case of compounds containing Mo_6 clusters the quantity χ_{VV}^0 can be identified with the orbital paramagnetic susceptibility of the isolated Mo_6 octahedron, in which 24 valence electrons saturate 12 two-centred metal-metal bonds. The high value of χ_{VV} found in Mo_6Te_8 therefore reflects the fact that in the telluride the Mo_6 octahedra retain strongly their molecular character, with minimum transfer of electrons from Mo to the chalcogen atoms.

[1] Ø. Fischer and M. B. Maple (eds), Superconductivity in Ternary Compounds, Springer, Berlin 1982.

[2] C. Roche, P. Pecheur, G. Toussaint, A. Jenny, H. Scherrer, and S. Scherrer, J. Phys.: Condensed Matter **10**, L333 (1998).

[3] R. W. Nunes, I. I. Mazin, and D. J. Singh, Phys. Rev. **B59**, 7969 (1999).

[4] R. Chevrel and M. Sergent, J. Solid State Chem. **6**, 433 (1973).

[5] O. K. Andersen, W. Klose, and H. Nohl, Phys. Rev. **B17**, 1209 (1978).

[6] Shu-Hui Cai and Chu-Wan Liu, J. Chem. Soc. Faraday Trans. **91**, 479 (1995).

[7] O. Pena, F. LeBerre, M. Sergent, R. Horyn, and A. Wojakowski, Physica C **235-240**, 771 (1994).

[8] R. Chevrel and M. Sergent, in [1].

[9] R. R. Gupta, in K. H. Hellwege and A. M. Hellwege (eds), Landolt-Boernstein Vol. II/16, Springer, Berlin 1986.

[10] A. M. Klogston, W. Jaccarino, and Y. Yafet, Phys. Rev. **134**, A650 (1964).

[11] H. J. Zeiger and G. W. Pratt, Magnetic Interactions in Solids, Clarendon Press, Oxford 1973.

[12] P. Fazekas, Lecture Notes on Electron Correlation and Magnetism, World Scientific, Singapore 1999.

[13] H. Nohl, W. Klose, and O. K. Andersen, in [1].

[14] K. Yvon, A. Paoli, R. Flükiger, and R. Chevrel, Acta Crystallogr. **B33**, 3066 (1977).

[15] K. Yvon in [1].

[16] L. Garbato, P. Manca, and A. Spiga, Nature Physical Science **239**, 156 (1972).

[17] L. Garbato and P. Manca, Chem. Phys. Letters **48**, 151 (1977).

[18] L. Pauling, The Nature of the Chemical Bond, 3rd ed., Cornell University Press, Ithaka 1960.