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Chevrel-phase solid solution $Mo_6 Se_{8-x}Te_x$. Study of its superconducting, magnetic and NMR properties

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Abstract

The Chevrel-phase solid solution Mo₆Se₈-Mo₆Te₈ was studied by X-ray diffraction, AC and DC magnetic susceptibility and ⁷⁷Se and ¹²⁵Te NMR spectroscopy. From the smooth evolution of the lattice parameters and superconducting critical temperatures, a progressive substitution of selenium atoms by tellurium is shown, on the whole range of composition $0 \le x \le 8$, in the formulation Mo₆Se_{8-x}Te_x: the unit-cell volume increases linearly because of the larger ionic size of tellurium, while T_c decreases rapidly (from 6.45 down to 0 K) because of the different formal oxidation states of the anions and a probable evolution of the Fermi level in the density of states. Results of magnetic susceptibility support this model and suggest the inhibition of the intrinsic metallic behavior with increasing x. The NMR spectra of the binaries Mo_6Se_8 and Mo_6Te_8 reveal two significant features, attributed to two different chalcogen positions in the R $\overline{3}$ symmetry. At low Se contents in $Mo_6Se_{8-x}Te_x$ (x = 7.5, 7 and 6), selenium first fills the two X(2) sites along the three-fold axis (2c positions), and then it becomes statistically distributed over the general 6f positions, leading to broad ⁷⁷Se NMR lines. On the other hand, substitution of Te atoms in Mo₆Se₈ seems to occur in a random way, creating large perturbations on the ¹²⁵Te NMR spectra, over the whole range of x. Theoretical analysis based on the presence of two anisotropic lines (of axial and non-axial symmetries, respectively) allowed us to estimate their anisotropy factors and to perfectly simulate the frequency response of both Mo₆Se₈ and Mo₆Te₈ binaries. Analysis of the Knight shift anisotropy leads us to conclude about the importance of the molybdenum z^2 molecular orbital contribution which controls the Mo-X dipolar interactions. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

* Corresponding author. Tel.: 33-2-99-28-67-57; fax: 33-2-99-63-57-04. The ternary molybdenum chalcogenides M_x^{n+} Mo₆X₈ (X = S, Se, Te), known as Chevrel phases [1], present very interesting superconducting properties, such as high transition temperatures and extremely important critical fields (e.g., 15 K and ~ 60 T, for PbMo₆S₈ [2]). In addition to this,

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when M is a rare-earth (RE) ion, the Chevrel-phase compounds may show unusual physical properties, in particular, the coexistence of magnetism and superconductivity [3].

In view of their similar superconducting behavior we can consider the binary chalcogenides Mo_6X_8 themselves as very interesting compounds (for instance, $T_c = 6.45$ K, $H_{c2} \sim 8$ T, for Mo₆Se₈ [2,4]). Their structure is based on the same network of Mo_6X_8 clusters as in the ternary Chevrel phases. Contrary to the selenide and telluride binaries, the sulfide compound Mo_6S_8 is a metastable phase which cannot be synthesized by direct combination of the elements; however, it can be prepared from a ternary phase (e.g., $Cu_x Mo_6 S_8$) by desintercalation methods, for instance, leaching the M ion by using a hydrochloric acid solution or by electrochemical oxidation [5,6]. Solid solutions between binaries have been well studied in the past: for instance, Chevrel et al. showed that the solid solution $Mo_6Se_8-Mo_6S_8$ can be prepared by direct synthesis from Mo_6Se_8 up to $Mo_6Se_4S_4$ [7], while Shelton studied the evolution of the critical temperature T_{c} of the binary selenide Mo₆Se₈ partially substituted either by S or by Te [8]. Very recent results have been published in single crystals of the $Mo_6Se_{8-x}S_x$ series obtained by desintercalation of nickel in Ni_vMo₆Se_{8-x}S_x crystals [9,10].

The valence-electron concentration (VEC) of the Mo_6 cluster plays an important role in the stability of the Chevrel phase. With only 20 electrons per Mo_6 cluster (3.33 electron per Mo cluster-atom) in the Mo_6S_8 compound, the Mo-d bonding level is located just below a forbidden energy gap. In the case of the selenide and telluride binaries, the covalent bondings are largely modified and the formal charges of Se and Te become smaller than the one of sulfur. This fact affects the number of electrons localized on the Mo₆ octahedron and causes the VEC to increase by $\frac{1}{6}$ and $\frac{2}{5}$ electrons/ cluster-atom, respectively [11]. As a consequence, the Mo-d band becomes more filled and the structure will stabilize; therefore, these binaries may form by direct synthesis. In the case of the ternary compounds, the structure is stabilized by the cation sublattice: valence electrons are transferred from the M atom towards the Mo₆X₈ cluster, increasing the degree of filling of the metal-metal bonding levels. This charge transfer scales down when going from sulfur to selenium and tellurium: the number of valence electrons which can be transferred is lower in the tellurides than in the selenides and sulfides, and it becomes much more difficult to insert divalent or trivalent cations in the Mo_6Te_8 sublattice.

Although many studies have been performed on the sulfide and selenide compounds, the Chevrel phase tellurides have not been the subject of a systematic research. In order to give a further insight into the telluride Chevrel phases, we started a systematic work on the pseudo-binary solid solution $Mo_6Se_{8-x}Te_x$, looking as an ultimate goal for the possibility to insert rare-earth ions in a telluriumbased network in the Chevrel-phase structure. Our NMR investigation is a first contribution, which may bring new elements to understand these systems.

2. Structural description

Since the discussion of our NMR data will be based mostly on structural features, we recall here below some basic facts concerning the crystal structure of these materials. The reader is referred to Ref. [5] for more details.

Molybdenum chalcogenides Mo_6X_8 crystallize in a hexagonal-rhombohedral symmetry (space group R3). These phases can be described as a stacking of Mo_6X_8 cluster units, each unit being a slightly distorted cube: the chalcogen atoms sit at the corners and the molybdenum atoms in the middle of the faces. All Mo atoms and 6 chalcogen atoms (hereafter called peripheral or X(1)) are in 6f positions, while the other two chalcogen atoms (axial or X(2)) are located at 2c positions on the three-fold axis. The Mo_6X_8 clusters are turned by an angle of about 25° around the ternary axis, resulting in close contacts between a Mo atom of one unit and the chalcogen atom of a nearby unit (Fig. 1).

Each Mo atom of a Mo₆ octahedral cluster is surrounded by five chalcogen atoms constituting a square-based pyramid. The base of the pyramid is in fact a face of a Mo_6X_8 unit, while the top is a chalcogen atom belonging to a neighboring



Fig. 1. View of 4 Mo_6X_8 units, showing axial (X(2)) and peripheral (X(1)) chalcogens, and strong (Mo–Mo) and (Mo–X(1)) bondings between nearby clusters. Units are rotated by ~ 25° with respect to the three-fold ($\overline{3}$) axis.

 Mo_6X_8 unit (Fig. 1). The X(1) atoms of a unit belong to the square faces and are also summits of six pyramids, while the X(2) atoms belong only to the square faces of the pyramid.

3. Experimental techniques and sample characterization

3.1. Synthesis and crystallochemistry

In a first step, molybdenum diselenide $MoSe_2$ and molybdenum ditelluride $MoTe_2$ were prepared in a quartz tube by direct reaction between metallic Mo (previously reduced under a hydrogen flow at 900°C) and the corresponding chalcogen. The reaction temperature was increased slowly during 3 days and stopped at 650°C (for $MoTe_2$) or 850°C (for $MoSe_2$).

In the next step, the binary compounds Mo_6Se_8 and Mo_6Te_8 and their solid solution Mo_6Se_{8-x} Te_x were prepared by sintering the corresponding molybdenum dichalcogenides with molybdenum metal. Before heating, the powders were thoroughly mixed, compacted into pellets, put inside alumina crucibles and sealed under secondary vacuum in a quartz tube. To avoid oxidation, all operations were performed in a glove box under dried and



Fig. 2. Lattice parameters $(a_{\text{hex}}, c_{\text{hex}})$ and unit-cell volume (V_{hex}) in the hexagonal symmetry for the Mo₆Se_{8-x}Te_x solid solution as a function of the tellurium x content (open symbols from Ref. [7]). Lines serve as a guide to the eye.

deoxygenated argon atmosphere. The sintering reaction was first carried out at 800°C for a day, followed by a heat treatement at 1200°C for 3 days and finally quenched in water. A series of samples of general formula $Mo_6Se_{8-x}Te_x$, for x = 0, 0.5, 1,2, 4, 6, 7, 7.5 and 8 was prepared. The resulting products were controlled by X-ray powder analysis.

X-ray powder diffraction patterns were obtained at room temperature using Cu-K_a radiation, and were indexed on the basis of a hexagonal unit cell similar to the well-known Mo₆Se₈ [12,13] and Mo₆Te₈ [12] crystal structures (space group R3). The lattice parameters are plotted in Fig. 2 as a function of the substitution rate x. Contrary to the metastable pseudo-binaries of Mo₆S_{8-x}Se_x type [5], the substitution of selenium by tellurium results in an almost linear increase of the unit-cell volume: in the former case, the weakness of the S-S intracluster bondings are responsible for an unstable Mo₆S₈ lattice, whereas in our case, close Se-Te contacts explain the linear increase of the lattice with the substitution rate. In the region of low x, a small decrease of the values of c_{hex} is observed, while the a_{hex} parameter seems to increase faster than an average linear behavior. At first sight, these deviations, also observed by other authors [7], may appear to be of no significance; however, as we shall see later (Section 4.2), it may also imply some real difficulties to insert a large chalcogen atom (like Te) in an otherwise stable Se₈ cage.

3.2. Superconducting properties

The solid solution $Mo_6 Se_{8-x}Te_x$ was also characterized from its superconducting point of view. A home-made AC susceptometer equipped with a mutual-inductance bridge [14,15] allowed us to measure the inductive transitions for samples of well-defined shape and volume. Full transitions were observed for all samples with $0 \le x \le 4$. Samples richer in tellurium could not be measured since their T'_{cs} [8] were beyond our temperature capabilities. Fig. 3 shows our values compared to those obtained by Shelton [8]; here again, a small increase of T_{c} at low x (within our error bars) may be of no significance. However, we should recall our recent results on slightly doped Mo₆Se₈ binaries, where a definite increase of $T_{\rm c}$, correlated with the ionic radius of the dopant, was systematically observed [4,16].

It is well known that superconductivity in the Chevrel phases is mostly due to the existence of a high Mo-d band density of states at the Fermi level, and that their relative positions may change with the oxidation state of both cations and anions. Calculations by Cai et al. [17] showed indeed, that the Fermi level in Mo₆Se₈ is situated at or very close to a peak of the density of states, while in the sulfide and telluride cases, it is situated near a minimum. In addition, in the case of Mo₆Te₈, the large increase of the VEC number provokes almost full occupation of the bonding states and, therefore, a semi-metallic behavior may be expected. As a result of these arguments, among the three binary chalcogenides, Mo_6Se_8 is at the optimum position from the point of view of their superconducting properties ($T_c = 1.8$, 6.45 and ~ 0 K, for Mo₆S₈ [5], Mo_6Se_8 [4] and Mo_6Te_8 [8], respectively).

Two effects may explain the T_c behavior at $x \rightarrow 0$, as observed in Fig. 3: from one side, a steric



Fig. 3. Superconducting critical temperature T_c as a function of x for the solid solution Mo₆Se_{8-x}Te_x (open symbols from Ref. [8]).

effect due to the larger size of tellurium compared to selenium. In this case, the position of the Fermi level may change and produce similar effects as in the doped binaries [4]. At the same time, the Mo-d bands become more filled because of the different charge transfers between Se and Te, leading to a decrease of T_c . These two effects may tend to compensate each other at low content of tellurium, resulting in quite constant T_c values in the range $0 \le x \le 1$.

At this point, it is good to recall results obtained in mixed clusters of the type $Mo_6Se_{8-x}Y_x$ [18], where the chalcogen (Se) was partially replaced by a Y halogen anion (Br or I). In that case, charge transfer effects (smaller valence of the anion) and halogen occupation on special crystallographic sites (axial Se(2) site) were invoked to explain an increase of T_c (up to 7.1 K for Mo_6Se_7Br and 7.6 K for Mo_6Se_7I). In our case, tellurium occupies random positions among the 8 corners of the pseudo-cubic cage (see Section 4.2) and it will produce a slight decrease of T_c for the same substitution rate ($T_c = 6.2$ K for Mo_6Se_7Te).

3.3. Magnetic susceptibility

DC magnetic susceptibility was measured in a SHE-VTS SQUID susceptometer, between 5 and



Fig. 4. Magnetic susceptibility, measured at 5 kOe, for 5 samples of the solid solution $Mo_6Se_{8-x}Te_x$.

300 K under an applied field of 5 kæ. At each measured temperature, the sample holder's contribution (of the order of 65-80% of the total signal) was subtracted, and the results were plotted as a function of temperature for 5 characteristic samples (Fig. 4). In most of the curves, a small rise of the paramagnetic signal was observed below 50 K, which was neglected in our subsequent discussion.

Two types of behaviors are apparent in Fig. 4, one for selenium-rich samples (Mo_6Se_8) and $Mo_6Se_6Te_2$), the other for tellurium-rich samples $(Mo_6Se_2Te_6 \text{ and } Mo_6Te_8)$. In the first group, the magnetic susceptibility is rather temperature-independent, with a tendency to increase linearly with decreasing T, in the range $100 \text{ K} \leq T \leq 300 \text{ K}$. This behavior can be interpreted in the same way as in some high- T_c high- H_{c2} ternary Chevrel phases, in which the Fermi level is situated near a peak in the density of states [2] (for instance, in $PbMo_6S_8$ or $LaMo_6Se_8$). Mo_6Se_8 could be assigned to such a group because of the relative position of the Fermi level [17] and also because of its $T_{\rm c}$ and $H_{\rm c2}(0)$ (6.45 K and 8 T, respectively), not far from those observed in the above-mentioned compounds (e.g., 11 K and 55 T, respectively, in LaMo₆Se₈ [19]).

The tellurium-rich samples (Mo_6Te_8 and $Mo_6Se_2Te_6$) showed a different thermal variation of the susceptibility, increasing with increasing temperature and suggesting the presence of a max-

imum above room temperature. The last sample, $Mo_6Se_4Te_4$, with equal amounts of selenium and tellurium anions, shows an intermediate temperature variation between these two behaviors, with an almost flat susceptibility in the range [100–300 K]. From these results it is quite tempting to suggest a smooth shift of T_{max} (that is, the temperature at which the magnetic susceptibility goes through a maximum) as a function of the tellurium concentration but we have no clear explanation at the moment for this particular effect.

The Pauli paramagnetism, as defined in our case by the room-temperature value $\chi(300 \text{ K})$, rapidly decreases with the increase of tellurium. This tendency suggests that the intrinsic metallic behavior observed for the Mo₆Se₈ binary is inhibited by the presence of tellurium, in agreement with our previous supposition of a semi-metallic behavior in the non-superconducting Mo₆Te₈. Preliminary NMR data obtained in the ⁹⁵Mo nucleus confirm these assumptions [20,21].

3.4. NMR experimental conditions

The as-sintered samples of the $Mo_6Se_{8-x}Te_x$ $(0 \le x \le 8)$ solid solution were thoroughly crushed to allow RF field penetration; about 3 grams of powder was then put into a pyrex tube and placed at the center of the RF coil. Room-temperature ⁷⁷Se and ¹²⁵Te NMR spectra were obtained on a BRUKER ASX 300 MHz spectrometer using the well-known Hahn spin-echo technique, that is a $\pi/2-\tau-\pi$ sequence ($\pi/2$ pulse of about 4 µs) which produces an echo signal in the receiving coil. The external applied magnetic field was 7 T and the expected resonance frequencies for the ⁷⁷Se and ¹²⁵Te nuclei (I = 1/2) were 57.2 MHz and 97.8 MHz, respectively. The accumulated echo signal was Fourier-transformed to give the absorption spectra, taking as time origin the top of the echo.

At this point we should stress that, due to the very broad lines observed in this work, several spectra had to be recorded for each compound at slightly different resonance frequencies (shifts of about 10 kHz each time): the resulting convoluted spectrum represents then the full response of the corresponding nucleus [22,23]. More details will be given in Section 4.

Standard materials used as chemical shift references for the ⁷⁷Se and ¹²⁵Te nuclei, were liquid solutions of H_2SeO_4 and K_2TeO_3 , respectively. Independent NMR analyses were made on pure selenium and tellurium elements, together with the two dichalcogenides (MoSe₂ and MoTe₂) used as starting materials for synthesis. In this way, any spurious peak which could appear in the NMR spectra could be identified as extrinsic or intrinsic features.

4. NMR results and discussion

4.1. ⁷⁷Se NMR in Mo_6Se_8 and ¹²⁵Te NMR in Mo_6Te_8

Figs. 5 and 6 show the ⁷⁷Se and ¹²⁵Te NMR spectra obtained at room temperature for the two binaries Mo_6Se_8 and Mo_6Te_8 . Because of the extremely broad lines, as stated in Section 3.4, each figure corresponds to the superposition of several spectra taken at different applied frequencies. In this way, the resulting convolution will better describe the expected characteristics, in particular the pronounced discontinuities in the low- and highfrequency regions, of each of the studied compounds.



Fig. 5. Room-temperature ⁷⁷Se NMR spectra of Mo_6Se_8 taken at slightly different resonant frequencies. Actual spectrum corresponds to the envelope.



Fig. 6. Room-temperature ¹²⁵Te NMR spectra of Mo_6Te_8 taken at slightly different resonant frequencies. Actual spectrum corresponds to the envelope.

The overall widths of the NMR lines of the pure binary phases are of comparable values (several tens of kHz for both Mo₆Se₈ and Mo₆Te₈). Several mechanisms may be responsible for such an important line width: first of all, the usual X-X and Mo-X dipolar interactions, which depend on the internuclear distances. Since the Mo-X distances are shorter than the X-X distances, we may expect that the Mo-X dipolar interaction would be dominant. However, the dipolar mechanism being also proportional to the gyromagnetic ratio (larger for Se and Te than for Mo) and to the natural abundance of the respective nuclei, the relative differences compensate and both Mo-X and X-X dipolar mechanisms retain the same order of magnitude. In any way, whatever the interaction may be, the dipolar mechanism is too weak to explain such broad lines. Another broadening mechanism, related to the distribution of powder grain shapes can also be considered. Here again, the low magnetic susceptibility of these compounds (Section 3.3) cannot justify any demagnetization broadening of the experimental lines. In fact, the main broadening mechanism expected in these compounds comes from the anisotropy of the paramagnetic (Knight)



Fig. 7. Simulated spectra of Mo_6Se_8 and Mo_6Te_8 , showing the positions of lines A and B and their superposition.

shift resulting, in a polycrystalline sample, from the molecular orientation with respect to the applied field. Since the electronic p-orbitals of the chalcogens are very sensitive to the local symmetry, as we shall see later, important shifts are then observed.

The experimental spectra obtained for the Mo₆Se₈ and Mo₆Te₈ binaries were fitted by standard techniques (WINFIT program, from BRUKER), in which two lines of different symmetries were assumed: line A, of axial symmetry, was assigned to the X(2) atoms situated on the ternary axis, while an anisotropic line B was ascribed to the six peripheral X(1) atoms. Integration of both lines was in the ratio 25:75, that is, on the expected relative occupancies for both crystallographic sites. Fig. 7 gives details about each of the simulated lines and their corresponding convolution. A perfect identification of the simulated spectra with the experimental data confirms the validity of our assumptions and, in particular, the formation of a "pseudo peak" at about 3100 ppm in the case of Mo₆Te₈. Table 1 gives details about the mathemat-

Table 1					
Parameters	of simulated	spectra	of Mo_6Se_8	and	$Mo_6 Te_8^{a}$

	Line	$\delta_{\rm iso}~{\rm (ppm)}$	η	⊿ (ppm)	S (%)
⁷⁷ Se in Mo_6Se_8 ¹²⁵ Te in Mo_6Te_8	A B A B	2690 3530 3040 4119	0.06 0.85 0.06 0.9	-510 770 +370 -1150	28.25 71.75 24.60 75.40

^aNote: (δ_{iso}) isotropic position; (Δ) anisotropy; (η) asymmetry; (S) surface under each peak.

ical parameters obtained from these fits, where δ_{iso} (in units of ppm) describes the line's isotropic position, Δ and η are the anisotropy and asymmetric parameters, respectively, and *S* (in percentage) corresponds to the area under each peak. Both lines get closer at lower temperature as δ_{B} decreases more rapidly than δ_{A} , which suggests an overall lattice contraction and a deformation of the Mo₆X₈ unit with a slight elongation along the three-fold axis [24].

A few other remarks should be made. Firstly, the Mo_6Te_8 spectrum is broader than the Mo_6Se_8 one since $[\delta_{B} - \delta_{A}]^{Mo_{6}Te_{8}} > [\delta_{B} - \delta_{A}]^{Mo_{6}Se_{8}}$, as it also occurs for the corresponding anisotropy factors. Secondly, line A of axial symmetry is qualitatively different in both compounds: while, in the selenide case, the anisotropy points toward decreasing values of δ_{iso} (i.e., in the direction of negative frequencies), in the telluride compounds it points in the opposite direction. This type of inversion, already encountered in other metals, has been explained by electronic arguments due to different fillings of the conduction band and the Fermi level position [25,26]. Such arguments may also apply to our case since, as we already discussed in Section 3.2, the $e_{\rm g}$ and $a_{\rm u}$ bands at the Fermi level may be basically different when going from the Mo₆Se₈ case to the Mo_6Te_8 compound. Finally, we should recall that the paramagnetic shift anisotropy is related to the hyperfine field due to the dipolar coupling between the nuclear and conduction electrons spins. In the case under consideration, of the two molybdenum molecular orbitals present at the Fermi level, (x^2-y^2) and z^2 , the latter is the most important one since it points toward the chalcogen atoms of the nearby unit. In this way, the Mo-X

bonding and its strongest covalent character in the case of Mo_6Te_8 , may be the principal reason for its largest anisotropy, compared to the Mo_6Se_8 case.

4.2. Solid solution

Figs. 8 and 9 show the ⁷⁷Se and ¹²⁵Te NMR spectra for the 9 samples of the solid solution $Mo_6Se_{8-x}Te_x$, x = 0, 0.5, 1, 2, 4, 6, 7, 7.5 and 8. For the sake of clarity, we have reproduced only the most relevant spectrum for each sample, and not the ensemble of spectra, as shown before in the case of the pure binaries.

The simplest way to describe the effects of partial chalcogen substitution in the $Mo_6Se_{8-x}Te_x$ solid solution is to look at the NMR spectra for very low concentration of substituent atoms. Of course, due to the very small amounts of the resonating nuclei (⁷⁷Se and ¹²⁵Te), the signal-to-noise ratio at both limits ($x \rightarrow 0$ and $x \rightarrow 8$) may look poor but good enough to perfectly describe the substitution mechanism between chalcogens.

4.2.1. ⁷⁷Se NMR

Fig. 8h and g show such spectra when only 0.5 and 1 atom are, on the average, substituted in the Mo₆Te₈ structure: only the narrow line A of axial symmetry is observed, centered at about the same position as the line attributed to the Se(2) atoms in the structure. From this result we can conclude that selenium atoms are first inserted at a preferential site in the 2c positions (i.e., along the three-fold axis), this occurring up to the composition $Mo_6Se_2Te_6$ (Fig. 8f). It is interesting to note that, at the lowest selenium contents, the anisotropy is of the Mo₆Te₈-type, that is, it points toward positive frequencies. Indeed, at these low concentrations of selenium, the conduction band and the position of the Fermi level are essentially similar to the Mo₆Te₈ case and, therefore, the sign of the Knight shift anisotropy is imposed by the tellurium environment and the corresponding VEC. At larger selenium content, the anisotropy must change its sign, to become negative, as explained before for the case of pure Mo₆Se₈.



Fig. 8. ⁷⁷Se NMR spectra for the solid solution $Mo_6 Se_{8-x}Te_x$. (a) x = 0, (b) x = 0.5, (c) x = 1, (d) x = 2, (e) x = 4, (f) x = 6, (g) x = 7, (h) x = 7.5.



Fig. 9. ¹²⁵Te NMR spectra for the solid solution $Mo_6 Se_{8-x}Te_x$. (a) x = 8, (b) x = 7.5, (c) x = 7, (d) x = 6, (e) x = 4, (f) x = 2, (g) x = 1, (h) x = 0.5.

When the two axial sites X(2) of the Mo_6Te_8 structure have been fully occupied by selenium atoms, other atoms start to occupy the X(1) sites at the general positions 6f of the structure. Since these 6 new sites are strictly equivalent, the progressive occupation is done in a random way, leading to very broad lines ($Mo_6Se_4Te_4$ and $Mo_6Se_6Te_2$, Fig. 8e and 8d, respectively), although their centers of gravity remain unchanged. The statistical character of the occupation of the 6 peripheral sites may also explain the approximate gaussian shape of the observed spectra. Finally, at composition $Mo_6Se_7Te_1$ (Fig. 8c) lines start to separate out, until the wellresolved ⁷⁷Se spectrum of Mo_6Se_8 is attained.

4.2.2. ¹²⁵Te NMR

The parallel situation, that is, the progressive increment of Te in the binary matrix Mo_6Se_8 , is shown in Fig. 9. However, as seen in Fig. 9h for the lowest substitution rate (x = 0.5), the ¹²⁵Te NMR

spectrum is already very broad, as if a random distribution of Se and Te takes place. Broad resonance lines with undistinguishable patterns continue to occur up to the composition $Mo_6Se_4Te_4$ (Fig. 9e). At further Te increment, lines start to split, giving place to the well-defined discontinuities of the Mo_6Te_8 binary; during this process, the overall line width stays quite constant.

Additionally, the presence of a noticeable peak in the tellurium resonance, centered at ~8000 ppm, is seen in Fig. 9h, which progressively disappears when the amount of Te increases. Different trials to identify such a peak by using the starting materials (Te metal or MoTe₂, for instance) were unsuccessful. On the other hand, if this peak was due to some extrinsic telluride phase, then it becomes difficult to understand why it disappears at higher concentration of tellurium. Therefore, our current hypothesis favors an intrinsic mechanism related to the insertion of a very big atom (i.e., Te) in the stable binary cluster formed by Mo and Se: the presence of 1 Te atom per Mo_6X_8 unit will considerably deform its almost perfect cubic shape, pushing the Te atom slightly outside the 2c or 6f crystallographic position. With further tellurium insertion, atoms will find more easily their expected atomic positions since the X_8 cage would have already adopted a deformed geometry. In this way, the "interstitial" position occupied by the Te atom, characterized by the NMR peak at ~ 8000 ppm, will progressively disappear at higher Te concentration. This mechanism will also explain the deviations to linearity observed in the evolution of the lattice parameters discussed in Fig. 2 and Section 3.1. Single-crystal structural refinement is in progress to investigate this point.

5. Conclusion

NMR spectroscopy is particularly interesting to study the microscopic aspects of the interplay between magnetism and superconductivity in the Chevrel-phase materials. The local modifications produced by the insertion of a third element (i.e., $M_x Mo_6 X_8$), or by the partial substitution at the chalcogen site can be monitored by the use of local probes. Up to now, NMR techniques have not been much used to study the Chevrel-phase compounds, despite the fact that many of the constituent atoms are appropriate nuclei for magnetic resonance (e.g., 77 Se, 125 Te, 95 Mo, ...).

In this work, we have chosen the simplest example in this family, that is, the binaries Mo_6Se_8 and Mo₆Te₈ and their solid solution, paying special attention to the way in which way the partial substitution Se \rightarrow Te takes place. An appropiate modelization allowed to identify the two different crystallographic sites, the peripheral X(1) and the axial X(2). When Se replaces Te in Mo₆Te₈, the substituent first fills the high-symmetry sites X(2) and then it becomes statistically distributed on the 6f positions. On the other hand, when Te replaces Se in Mo₆Se₈, it occupies randomly all the 8 sites of the Mo₆X₈ structure, creating large perturbations of the NMR spectra over the whole range of x. The evaluation of all the parameters used in these fits allowed us to interpret the paramagnetic shift anisotropy as being mainly due to the Mo z^2 molecular orbitals. In addition, the relative position of the Fermi level with respect to the Mo-d band density of states, which explains important changes in the physical properties of this series as a function of x (e.g., T_c , magnetic susceptibility, electrical transport, etc.) may also take into account the different signs of the anisotropy between Mo₆Se₈ and Mo₆Te₈.

Further work is in progress, including the 95 Mo NMR, the thermal evolution of the anisotropic shifts or the importance of the cation lattice (i.e., M = RE). Evidently, a parallel characterization of these materials, as done in this work, is essential to verify their quality, but also to understand other important NMR phenomena, such as [Knight shift-magnetic susceptibilty] correlations or spinlattice relaxation mechanisms.

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