

Structural phase transition in GaMo_4S_8 by X-ray powder diffraction

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*Dedicated to Professor Hans Georg von Schnering
on the occasion of his 60th birthday*

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Abstract. GaMo_4S_8 transforms at $T_t = 45(5)$ K from a cubic high-temperature modification with ordered defect spinel structure (space group $F\bar{4}3m$, $a = 9.7356(2)$ Å at 300 K) to a rhombohedrally distorted low-temperature modification ($R3m$, $a_{\text{rh}} = 6.8506(2)$ Å, $\alpha_{\text{rh}} = 60.533(1)^\circ$ at 8 K). The transition is of first order, shows a hysteresis of about 4 K, and leaves about 30% of the cubic phase untransformed. Lattice parameters as a function of temperature are reported between 8 K and 300 K, and structure refinements are performed by the Rietveld method from data recorded on a Guinier diffractometer at 8 K and 300 K. The tetrahedral Mo_4 clusters expand during the phase transition at one of their triangular bases, $[\text{Mo} - \text{Mo}]_A = 2.814(3)$ Å at $T = 300$ K; $2.89(1)$ Å at $T = 8$ K, while the other intra-cluster distances, $[\text{Mo} - \text{Mo}]_B = 2.814(3)$ Å at $T = 300$ K; $2.81(2)$ Å at $T = 8$ K, and inter-cluster distances, $[\text{Mo}_4 - \text{Mo}_4] = 4.070(3)$ Å at $T = 300$ K; $4.02 - 4.04(2)$ Å at $T = 8$ K, remain approximately constant.

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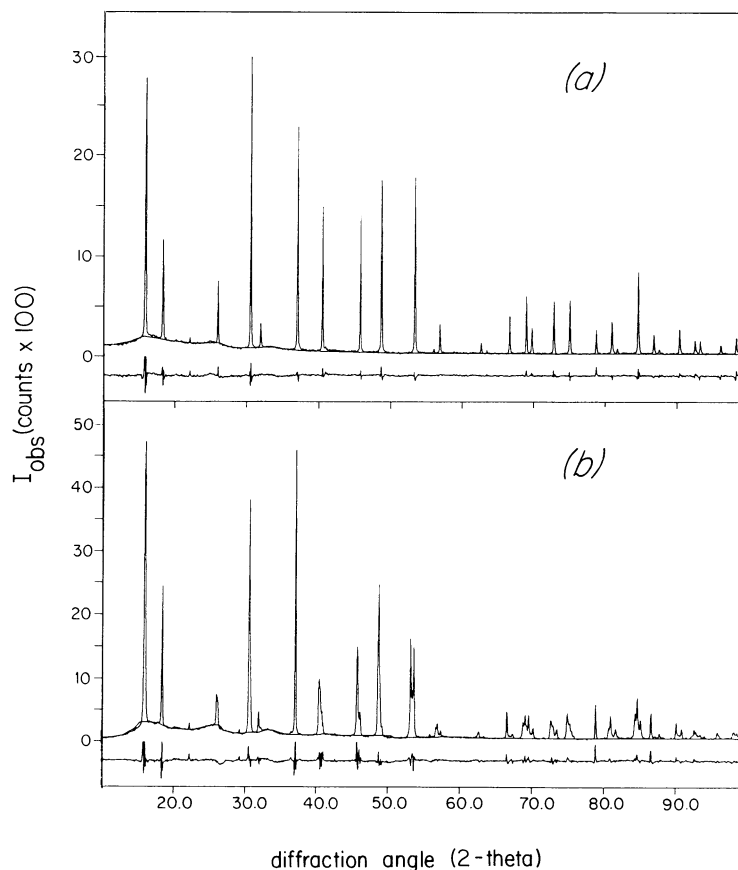


Fig. 1. Observed (top) and difference X-ray diffraction patterns (bottom) of GaMo_4S_8 (a) at 300 K, (b) at 8 K, ($\lambda = 1.54056 \text{ \AA}$).

Introduction

Semiconducting GaMo_4S_8 shows heavy fermion behaviour, is metamagnetic with a critical field H_c of 5 KG, and orders ferromagnetically at $T_c = 19.5 \text{ K}$ (Rastogi and Wohlfarth, 1987; and references therein). The compound was first reported by Barz (1973) and initially described as a gallium deficient spinel. Its structure was characterized from X-ray powder diffraction at room temperature by Vandenberg and Brasen (1975), and from single-crystal X-ray diffraction by Perrin et al. (1975). The space group symmetry found ($F\bar{4}3m$) was lower than that of spinel ($Fd\bar{3}m$). The gallium atoms were ordered at one of the four-fold tetrahedral sites ($4a$) that derive from the eight-fold metal A site ($8a$) in the normal spinel, AB_2X_4 , the other tetrahedral sites ($4c$) being empty. The molybdenum

atoms were shifted away from the spinel B sites and formed regular tetrahedral Mo₄ clusters with metal-metal bonds that were much shorter within the clusters ($[\text{Mo}-\text{Mo}]_{\text{intra}} = 2.823 \text{ \AA}$) than between the clusters ($[\text{Mo}-\text{Mo}]_{\text{inter}} = 4.056 \text{ \AA}$) (Perrin et al., 1975) (for a drawing see Fig. 1 of Vandenberg and Brasen, 1975). A structural instability was first reported from specific-heat measurements by Shamrai et al. (1982), and by Ben Yaich et al. (1984), indicating a first-order transition at $T_l = 46.5 \text{ K}$, i.e. above the magnetic transition at $T_c = 19.5 \text{ K}$. The transition was later confirmed from X-ray powder diffraction by Shamrai and Leitus (1987), who proposed for the low-temperature modification rhombohedral lattice symmetry and the likely space group $R3m$. A structure refinement based on that symmetry was recently reported from low-resolution neutron powder diffraction data at 35 K and 3 K in the thesis of Ben Yaich (1989). In order to characterize the transition further, high-resolution X-ray data were collected as a function of temperature.

Experimental

The preparation of the GaMo₄S₈ sample was described in the work by Perrin et al. (1975). Single crystals were grinded to a fine powder (grain size = 1–10 μ) and put into a Guinier diffractometer equipped with a closed-cycle helium refrigerator (Ihringer, 1982). A series of spectra was recorded in the temperature range between 8 K and 300 K, at intervals of about 40 K at high temperature (HT) and of about 4 K at low temperature (LT), during 3 h for each temperature, in the theta range between 5°–50° θ , and in steps of 0.005° θ , by using monochromated [Ge(111)] CuK α_1 radiation and silicon ($a = 5.4308 \text{ \AA}$) as an internal standard (linear interpolation between 6 silicon reflexions). Lattice parameters were refined from measured and corrected line positions by using the LATCON program (D. Schwarzenbach, 1966). Atomic parameters were refined from patterns recorded during 48 h at 300 K and 8 K, respectively, for the HT and LT modification by using the Rietveld (1969) method. The program used (Wiles and Young, 1981) was modified for the correction of the Lorenpolarisation factor applicable for Guinier geometry. The atomic starting parameters used for the cubic HT modification [$F\bar{4}3m$; Mo, S(1) and S(2) in 16 e ; Ga in 4 a] were those reported from single-crystal X-ray diffraction by Perrin et al. (1975), and for the rhombohedral LT modification [$R3m$; Mo(1), S(1), S(3) and Ga in 1 a ; Mo(2), S(2) and S(4) in 3 b] those reported from the neutron experiment (Ben Yaich, 1989).

Results and discussion

As shown in Fig. 1, the X-ray diffraction pattern at 8 K differs significantly from that at room-temperature. Most diffraction lines are split or

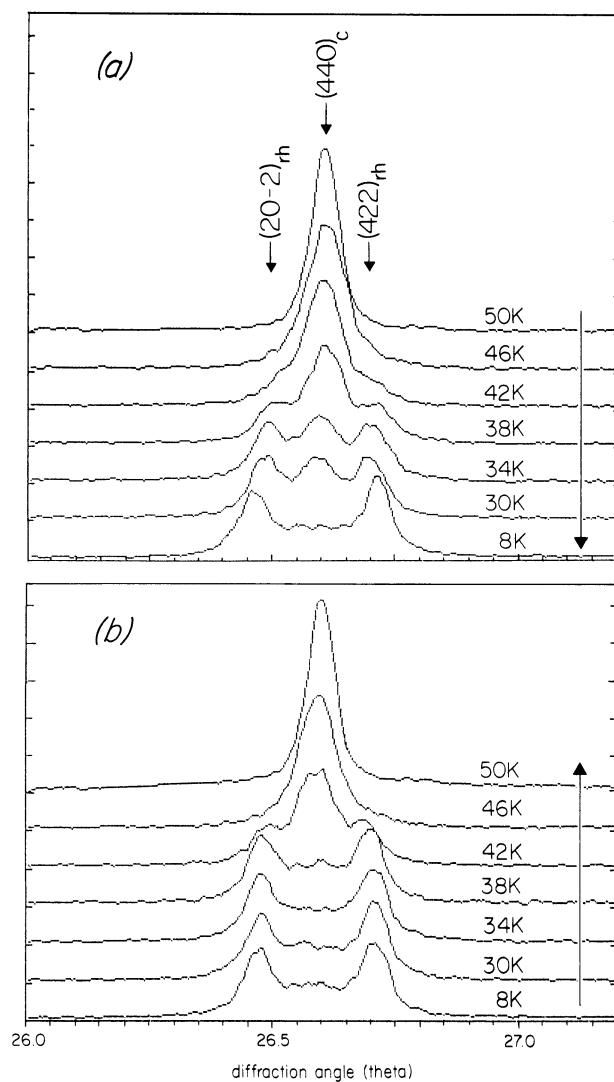


Fig. 2. X-ray diffraction pattern of GaMo₄S₈ in a selected θ -range as a function of temperature, during cooling (a) and heating (b).

broadened, thus confirming the structural phase transition. The transition can be studied in detail from a plot of the partial profiles ($\theta = 26.0^\circ - 27.2^\circ$) recorded in the temperature range between 30 K and 50 K at various temperatures during cooling (Fig. 2a) and heating (Fig. 2b). Upon cooling, the transition starts between 38 K and 42 K, as can be seen from the broadening of the $(4\ 4\ 0)_c$ reflexion of the cubic modification, and the

appearance of two satellite peaks corresponding to the $(2\ 0\ -2)_r$ and $(4\ 2\ 2)_r$ reflexions of the rhombohedral modification. As the temperature is further decreased the intensity of the $(4\ 4\ 0)_c$ reflexion decreases and those of the two satellites increase. Interestingly, even at 8 K, the $(4\ 4\ 0)_c$ reflexion has not totally disappeared, indicating that the phase transition is not complete. Upon heating, the transition back to the cubic modification is completed at 46 K only. This hysteresis (about 4 K) indicates that the transition is of first-order, although the change of symmetry ($R3m$ is a maximal non-isomorphic subgroup of $F\bar{4}3m$) would allow the phase transition to be of second-order. Lattice parameters as a function of temperature are shown in Fig. 3. At the transition temperature $T_l = 45(5)$ K the rhombohedral cell edge and cell angle vary discontinuously from $a_{rh} = 6.8768(3)$ to $6.8527(3)$ Å, and from $\alpha_{rh} = 60.00(-)^\circ$ to $60.48(1)^\circ$, respectively, i.e. the lattice contracts along the threefold axis. The variation of the cell volume, V_{rh} , is less pronounced and shows only a small anomaly at 50 K, i.e. at a temperature slightly above T_l .

Results of the structure refinements at 8 K and 300 K are summarized in Table 1 and compared with earlier X-ray single-crystal (Perrin et al., 1975) and neutron powder (Ben Yaich, 1989) diffraction data. The atomic parameters obtained at 300 K are less precise than those of the single-crystal study, but do not differ by more than two standard deviations from the latter. Those obtained at 8 K are in agreement with, and of similar accuracy than, the neutron powder data obtained at 3 K. Their estimated standard deviations (e.s.d.'s) are larger by a factor of 4 than those of the 300 K data. This is presumably due to the contamination of the LT patterns by the untransformed cubic parent phase. In the previous neutron work that phase was not included in the refinements. In the present X-ray work it was included, but the refinement suffered from strong parameter correlations. The amount of cubic phase as estimated from the ratio of the two scale factors was about 30%.

A representation of the partial structure perpendicular to the threefold axis is shown in Fig. 4, and the interatomic distances as calculated with the BONDLA program of the XTAL system (Hall and Stewart, 1989) are summarized in Table 2. Significant differences between the HT and LT modification (see values marked by stars) occur mainly with the Mo–Mo intracluster bond distances (see cube shaped Mo₄S₄ group marked C₁ in Fig. 4) and the S–S contact distances within the empty sulphur tetrahedron (marked T₂ in Fig. 4), and less with the Mo–Mo intercluster distances (see Mo₄S₄ group marked C₂) and the Ga–S bond distances within the Ga centred sulphur tetrahedron (marked T₁). As to the Mo–Mo intra-cluster distances at 300 K ($[\text{Mo}–\text{Mo}] = 2.814(3)$ Å) they split in two non-equivalent distances at 8 K, one between the axial Mo1 and the triangular group of peripheral Mo2 atoms that does not much change ($[\text{Mo}–\text{Mo}_A] = 2.81(2)$ Å), and the other within the triangular group of Mo2 atoms that

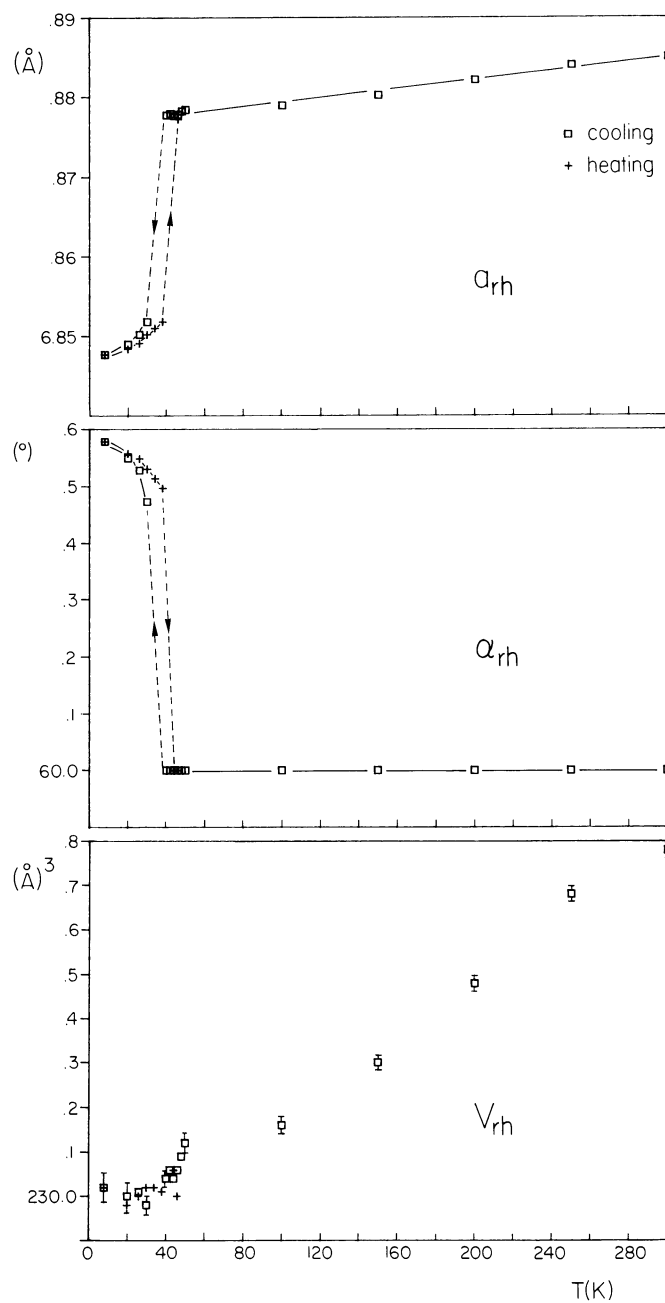


Fig. 3. Lattice parameters of GaMo_4S_8 as a function of temperature. Above the phase transition temperature the face centered cubic cell is described with the rhombohedral subcell; $a_{rh} = a_c/\sqrt{2}$, $\alpha_{rh} = 60^\circ$.

Table 1. Refinement results of GaMo₄S₈ at 300 K and 8 K.a) At 300 K (70 K) (space group $F\bar{4}3m$)

Technique	X-ray powder		Neutron powder		X-ray single crystal	
Reference	This work		Ben Yaich (1989)		Perrin et al.	
Lattice parameters	(300 K)		(70 K)		(1975) (300 K)	
	$a = 9.7356(2) \text{ \AA}$		$a = 9.727(-) \text{ \AA}$		$a = 9.73(-) \text{ \AA}$	
Atom Position	x	$B_{\text{iso}} [\text{\AA}^2]$	x	$B_{\text{iso}} [\text{\AA}^2]$	x	$B_{\text{iso}} [\text{\AA}^2]$
Mo (16e)	0.3978(2)	0.64(7)	0.3972(2)	0.7(6)	0.3974(5)	0.34
S1 (16e)	0.6343(5)	0.72(15)	0.638(2)	3.0(7)	0.6343(2)	0.69
S2 (16e)	0.1345(5)	0.72(15)	0.1353(6)	5.1(10)	0.1350(2)	0.43
Ga (4a)	0	1.0(3)	0	1.1(13)	0	0.45
$R_p = 10.3\%$	Total number of refined parameters: 16					
$R_{wp} = 13.3\%$	Number of atomic parameters: 6					
$R_{exp} = 8.0\%$	Number of profile parameters: 6					
$R_1 = 4.0\%$						

b) At 8 K (space group $R3m$)

Technique	X-ray powder			Neutron powder		
Reference	This work			Ben Yaich (1989)		
Lattice parameters	$a_{rh} = 6.8506(2) \text{ \AA}$			$a_{rh} = 6.851(-) \text{ \AA}$		
	$\alpha_{rh} = 60.533(1)^\circ$			$\alpha_{rh} = 60.54(-)^\circ$		
Atom Position	x	z	$B_{\text{iso}} [\text{\AA}^2]$	x	z	$B_{\text{iso}} [\text{\AA}^2]$
Mo1 (1a)	0.399(1)	x	0.1(1)	0.400(1)	x	—
Mo2 (3b)	0.396(1)	0.814(1)	0.1(1)	0.397(1)	0.812(2)	—
S1 (1a)	0.636(2)	x	0.3(2)	0.634(2)	x	—
S2 (3b)	0.642(3)	0.088(3)	0.3(2)	0.636(2)	0.101(3)	0.10(35)
S3 (1a)	0.135(2)	x	0.3(2)	0.132(2)	x	—
S4 (3b)	0.138(3)	0.592(3)	0.3(2)	0.138(2)	0.598(3)	—
Ga (1a)	0	x	0.6(3)	0	x	—
$R_p = 11.8\%$	Total number of refined parameters: 22					
$R_{wp} = 15.4\%$	Number of atomic parameters: 12					
$R_{exp} = 7.0\%$	Number of profile parameters: 6					
$R_1(\text{rhombohedral phase}) = 7.6\%$						
$R_1(\text{cubic phase}) = 8.0\%$						

increases substantially ($[\text{Mo} - \text{Mo}]_d = 2.89(1) \text{ \AA}$). The Mo–Mo distances between the Mo₄ clusters remain approximately constant: $[\text{Mo}_4 - \text{Mo}_4] = 4.070(3) \text{ \AA}$ (HT), $4.02 \text{ \AA} - 4.04(2) \text{ \AA}$ (LT). This is also true for the Mo–S bond distances. In the LT structure those capping the triangular faces of the Mo₄ cluster, $[\text{Mo} - \text{S}]_{av} = 2.41(2) \text{ \AA}$ (see C₁ in Fig. 4) are significantly shorter than those linking these clusters, $[\text{Mo} - \text{S}]_{av} = 2.58(2) \text{ \AA}$ (see C₂ in

Table 2. Bond distances, and S–S contact distances (Å) up to 4.1 Å, in GaMo₄S₈ at 300 K and 8 K.

300 K (<i>F</i> $\bar{4}3m$)			8 K (<i>R</i> 3 <i>m</i>)							
Mo	3S(1)	2.344(5)	Mo(1)	3S(2)	2.41(2)*	C ₁				
	3S(2)	2.602(5)		3S(4)	2.58(3)	C ₂				
	3Mo	2.814(3)		3Mo(2)	2.81(2)	C ₁				
	3Mo	4.070(3)		3Mo(2)	4.04(2)	C ₂				
S(1)	3Mo	2.344(5)	Mo(2)	S(1)	2.38(3)	C ₁				
				2S(2)	2.38(3)	C ₁				
				S(3)	2.57(2)	C ₂				
				2S(4)	2.57(3)	C ₂				
	3S(1)	3.186(7)	3.698(7)	Mo(1)	2.81(2)	C ₁				
				2Mo(2)	2.89(1)*	C ₁				
				2Mo(2)	4.02(1)	C ₂				
				Mo(1)	4.04(2)	C ₂				
				S(1)	3Mo(2)	2.38(3)	S(1)	3Mo(2)	2.38(3)	C ₁
							3S(2)	3.13(4)	T ₂	
							3S(2)	3.72(3)	C ₁	
							S(2)	2Mo(2)	2.38(2)	Mo(1)
2S(2)	3.08(3)*	T ₂								
S(1)	3.13(3)*	T ₂								
S(1)	3.72(3)	C ₁								
S(2)	Ga	2.268(5)	S(3)	2S(2)	3.82(2)*	C ₁				
				Ga	2.26(3)	T ₁				
				3Mo	2.57(2)	C ₂				
				3S(4)	3.15(4)	C ₂				
				3S(4)	3.70(3)	T ₁				
				S(4)	Ga	2.30(2)	Ga	2.30(2)	T ₁	
							2Mo(2)	2.57(2)	C ₂	
							Mo(1)	2.58(2)	C ₂	
2S(4)	3.13(2)	C ₂								
S(3)	3Mo(2)	2.57(2)	S(3)	3.15(3)	C ₂					
			S(3)	3.70(3)	T ₁					
			2S(4)	3.77(2)*	T ₁					
			S(3)	3S(4)	2.26(3)	Ga	2.26(3)	T ₁		
3S(4)	2.30(2)	T ₁								

Values of the LT modification marked by a star differ by more than 3 sigmas from the equivalent ones in the HT modification. The last column refers to the structural units in Fig. 4.

Fig. 4), similar to those in the HT structure (C₁: [Mo–S] = 2.34(5) Å, C₂: [Mo–S] = 2.602(5) Å). The expansion of the triangular group of Mo₂ atoms in C₁ and the contraction of the empty tetrahedron T₂ is consistent with the opening of the rhombohedral lattice angle α_{rh} .

As to the origin of the structural phase transition our results suggest an electronic instability associated with the Mo₄ cluster. The cluster contains

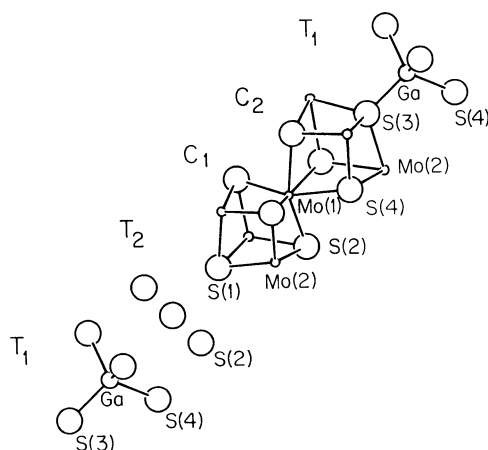


Fig. 4. Partial structure of GaMo₄S₈ along the three-fold axis, represented as a linkage of two types of Mo₄S₄ groups (noted C₁ and C₂) and two types of sulfur tetrahedra, one centered by Ga (T₁), and the other empty (T₂).

formally 11 valence electrons with one unpaired electron. They are localized on the cluster, as suggested from the large distance between the clusters and the observed semiconducting behaviour (Ben Yaich, 1989). During the phase transition the distances between the clusters do not much change and the compound still shows semiconducting behaviour with one unpaired electron per Mo₄ cluster. This situation differs from that in another class of structurally unstable Mo cluster compounds, i.e. MMo₆S₈ (M = Ca, Sr, Ba, Eu). At room temperature the latter are metallic and contain (nearly regular) octahedral Mo₆ clusters that are relatively close to each other ($[\text{Mo}_6 - \text{Mo}_6] = 3.2 \text{ \AA}$). At low temperature they undergo a triclinic distortion that leads to the opening of a gap in a partially filled band, and, for some compounds such as M = Eu (Kubel and Yvon, 1990, and references therein), and M = Ca_{1.0} (Geantet et al., 1987), to semiconducting behaviour. The transition in these compounds is usually complete. The reason why GaMo₄S₈ transforms only partially is not yet clear. It could be due to hysteresis, but sample stress, non-stoichiometry or inhomogeneity could also play a role.

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References

- Barz, H.: New ferromagnetic molybdenum spinels. *Mater. Res. Bull.* **8** (1973) 983–988.

- Ben Yaich, H., Jegaden, J. C., Potel, M., Chevrel, R., Sergent, M.: Nouveaux chalcogénures mixtes $\text{GaMo}_4(\text{XX}')_8$ ($X = \text{S, Se, Te}$) à clusters tétraédriques Mo_4 . *J. Solid State Chem.* **51** (1984) 212–217.
- Ben Yaich, H.: Chalcogénures ternaires à clusters tétraédriques Me_4 ($\text{Me} = \text{V, Nb, Ta, Mo, Re}$), cristalllogénèse, études structurales et propriétés physiques, thèse No B503269, Université de Rennes (1989)
- Geantet, C., Padiou, J., Pena, O., Sergent, M., Horyn, R.: Evidence of superconductivity in $\text{Ca}_x^{2+}\text{Mo}_6\text{S}_8$ single crystals at normal pressure. *Solid State Commun.* **64** (1987) 1363–1368.
- Hall, S. R., Stewart, J. M.: Eds., XTAL2.6 User's Manual. Universities of Western Australia and Maryland (1989).
- Ihringer, J.: An automated low-temperature Guinier X-ray diffractometer and camera. *J. Appl. Crystallogr.* **15** (1982) 1–4.
- Kubel, F., Yvon, K.: Structural phase transition in Chevrel phases containing divalent metal cations. II. Structure refinement of triclinic EuMo_6S_8 and BaMo_6S_8 at low temperature. *Acta Crystallogr.* **C46** (1990) 181–186.
- Perrin, C., Chevrel, R., Sergent, M.: Sur un nouveau cluster tétraédrique de molybdène dans les chalcogénures MMo_4S_8 ($M = \text{Al, Ga}$), GaMo_4S_8 et dans les thiohalogénures MoSX ($X = \text{Cl, Br, I}$). *C. R. Acad. Sci. Paris* **280C** (1975) 949–951.
- Rastogi, A. K., Wohlfarth, E. P.: Magnetic field-induced transitions in the Mo_4 clusters compounds GaMo_4S_8 and GaMo_4Se_8 showing heavy fermion behaviour. *Phys. Stat. Solidi (b)* **142** (1987) 569–573.
- Rietveld, H. M.: A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2** (1969) 65–71.
- Schwarzenbach D.: (1966) Private communication.
- Shamrai, V. F., Leitus, G. M.: Low temperature structural transitions and magnetic properties of GaMo_4S_8 type compounds with defect spinel structure. *Sov. Phys. Solid State* **29** (1987) 1312–1315.
- Shamrai, V., Mädege, H., Mydlarz, T., Leitus, G.: Low-temperature properties of $\text{Ga}_{0.5}\text{Mo}_2\text{S}_4$. *J. Low-Temp. Phys.* **49** (1982) 123–133.
- Vandenberg, J. M., Brasen, D.: Structural behaviour of the ferromagnetic spinels $\text{Al}_x\text{Mo}_2\text{S}_4$ and $\text{Ga}_x\text{Mo}_2\text{S}_4$ containing tetrahedral clusters of molybdenum atoms. *J. Solid. State Chem.* **14** (1975) 203–208.
- Wiles, D. B., Young, R. A.: A new computer program for Rietveld analysis of X-ray powder diffraction patterns. *J. Appl. Crystallogr.* **14** (1981) 149–151.