

The effect of high pressures on the magnetic properties of chromium tellurides

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On the basis of experimental investigations (Grazhdankina *et al.*, 1961) of the Curie temperature T_C of chromium telluride CrTe and of the solid solutions $\text{CrTe}_{1-x}\text{X}_x$ (where X = S, Se, or Sb) under high pressures it could be expected that two mechanisms of exchange coexist in chromium tellurides: (i) indirect antiferromagnetic (AF) exchange of localised electrons via the nonmagnetic ion, and (ii) interaction of shared electrons in the narrow 3d band; the energy of the latter is dominant and governs the value of T_C .

To establish the validity of this hypothesis we have investigated chromium telluride in which a monoclinic distortion of the unit cell was produced by heat treatment. The distortion results in the enhancement of the AF-superexchange and the appearance of noncollinear magnetic structure at low temperatures. In this case the alloy has a magnetic phase transformation at the temperature of $T_s = 110$ K connected with the transition of the noncollinear magnetic structure into a ferromagnetic one, and a maximum is observed in the temperature dependence of the magnetisation curve, $\sigma(T)$ (Grazhdankina *et al.*, 1974).

The results of measurements of magnetisation under pressures up to 13 kbar are shown in figure 1. Figure 2 shows the dependence of T_C and T_s on pressure. It can be seen that at $T < T_s$ the value of σ decreases with increasing pressure and the derivatives $dT_s/dP = 6$ K kbar⁻¹ and $dT_C/dP = -5.9$ K kbar⁻¹ are of opposite sign. These results can be interpreted in terms of the coexistence of the two aforementioned exchange mechanisms. According to Goodenough (1968) AF superexchange increases with pressure since the latter causes an increase of the transfer integral b and the AF exchange energy is proportional to b^2 . This leads to an increase of T_s and a decrease of σ with increasing pressure. The decrease of T_C with increasing pressure is due to a change of the interaction between the electrons in the narrow 3d band. The large negative value of dT_C/dP is caused by the decrease of electron density near the Fermi surface connected with the increase of the bandwidth at high pressures.

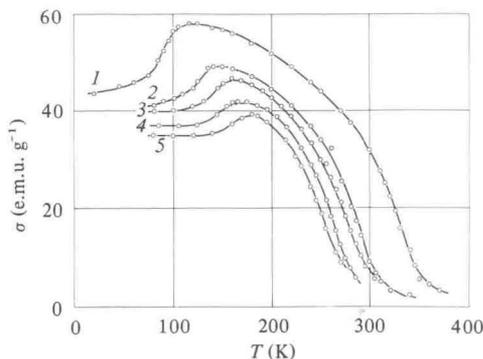


Figure 1. Temperature dependence of specific magnetisation of CrTe in a field of 8 kOe at hydrostatic pressures of: 1 0 kbar; 2 5.8 kbar; 3 0.3 kbar; 4 11.4 kbar; 5 12.9 kbar.

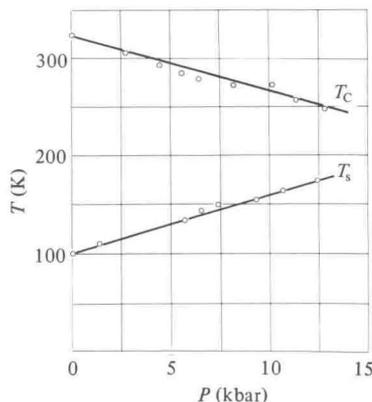


Figure 2. Pressure dependence of magnetic transformation temperatures T_C and T_s in chromium telluride.

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Investigation of the phase transition in magnesium stannide under hydrostatic pressure by the Mössbauer effect and electric resistance

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We are reporting here preliminary results of an investigation of the phase transition in Mg_2Sn under hydrostatic pressure, with benzene as the pressure transmitting medium. Our results disagree with the data of Möller (1968) who used Bridgman anvils. Electric resistance measurements show that the experimental results depend on the type of the applied pressure (figure 1). The same is found with the Mössbauer method. With Bridgman anvils (Möller, 1968) a single Mössbauer line is obtained at each pressure; under hydrostatic pressure a broadening and asymmetry of Mössbauer Mg_2Sn lines are observed in the pressure region 30-47 kbar. x-Ray data (Dyuzheva *et al.*, 1972), indicate that the pressure range 25-50 kbar corresponds to a two-phase Mg_2Sn system where the new and the old phases coexist.

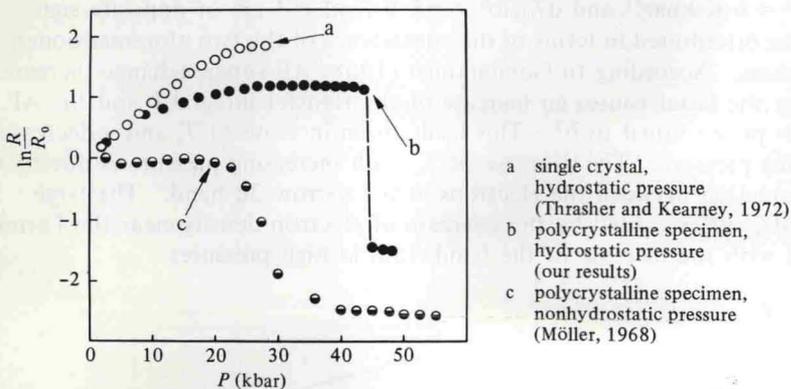


Figure 1. Pressure dependence of the electric resistance of Mg_2Sn under different conditions.

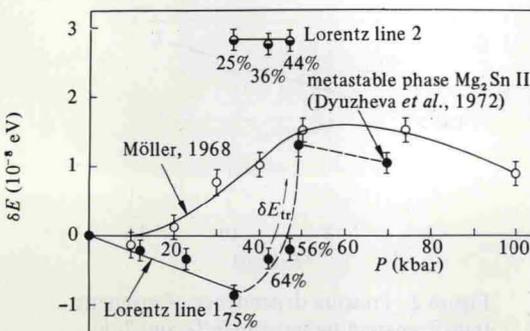


Figure 2. Shift of the Mössbauer lines, δE , for Mg_2Sn under pressure. The percentages shown relate to the areas of lines 1 and 2.

We have computed Mössbauer spectra from two Lorentz lines. The isomer shift is shown in figure 2. We suggest that line 1 corresponds to the crystal phases Mg_2Sn I (0–35 kbar) and II (>35 kbar), and the steep change of the isomer shift δE_{tr} provides information on the change of the electronic configuration of Mg_2Sn at the phase transition. The change in the isomer shift δE_{tr} reflects the increase of electron density at Sn nuclei, which is a usual feature of a first-order phase transition. The decrease of δE preceding the phase transition is also a common characteristic for all the tin systems studied so far and shows a decrease of electron density at Sn nuclei before transition.

It is too early to reach a definite conclusion about the nature of line 2 which occurs in the transition pressure region, but it is possible that this line is related to some intermediate state of the Mg_2Sn system present at the grain boundaries of Mg_2Sn I and Mg_2Sn II phases. It should be remembered that the Mössbauer effect can show up both crystalline and amorphous systems.

References

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Investigation of S-state splitting the gadolinium ion in fluorite crystals by ESR and ENDOR at high pressure

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Splitting of the S ground state (with orbital angular momentum $L = 0$) of paramagnetic ions has been investigated by many workers since the appearance of the first paper on the subject by Van Vleck and Penny (1934). Watanabe (1957) specifies twelve processes which can lead to the splitting of the S state. Powell *et al.* (1960) and Gabriell *et al.* (1961) consider both odd and even perturbation processes by the crystalline field potential Dq . The idea of identifying actually occurring processes with the aid of experiments under high hydrostatic pressures was put forward by Watanabe (1960).

We have studied the influence of high pressure on the electron spin resonance (ESR) spectra of the gadolinium ion in fluorite crystals. The logarithmic derivative, n , of the cubic splitting parameter b_4 with respect to the lattice parameter a is equal to 7.0 ± 0.3 for CaF_2 (Kasatochkin *et al.*, 1973). The quantity n can be regarded as the exponent in the relationship

$$b_4 \propto a^{-n} \quad (1)$$

approximating the behaviour of b_4 as a function of a .

The value of the exponent n is of use only when the local compressibility of the paramagnetic complex is known. In order to determine the local compressibility we have made high-pressure determinations by electron–nuclear double resonance (ENDOR) on fluorine ligands (Kasatochkin and Yakovlev, 1975). The logarithmic derivative m of the anisotropic hyperfine coupling parameter A_p with ligands of the first coordination shell with respect to the lattice parameter a is equal to 2.26 ± 0.1 . The quantity m has a similar meaning to the quantity n in equation (1). The difference between the value of m and the dipole–dipole value $m = 3$ is related to the difference between local and bulk compressibilities, if we neglect the small contribution of anisotropic exchange.

The value of n corrected for the difference between local and bulk compressibilities is 9.3. This value is reasonably close to the value of 10 yielded by the point-charge model for the case when the cubic splitting parameter b_4 is proportional to the square of the crystalline field parameter Dq :

$$b_4 \propto (Dq)^2.$$

Thus, using the $\text{CaF}_2:\text{Gd}^{3+}$ system as an example, we have solved the problem posed by Watanabe (1960).

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High pressure polymorphs of niobium dichalcogenides

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Specimens of niobium disulphide, niobium diselenide, and niobium ditelluride were synthesised from stoichiometric mixtures of the components at 90 kbar (table 1). At 1200–1350°C two new phases were obtained: NbS_2 II and NbSe_2 II. All lines on the powder photographs can be assigned on the basis of a hexagonal unit cell with parameters $a = 3.33 \text{ \AA}$, $c = 23.8 \text{ \AA}$, $c/a = 4 \times 1.787$ (NbS_2 II); and $a = 3.46 \text{ \AA}$, $c = 24.8 \text{ \AA}$, $c/a = 4 \times 1.791$ (NbSe_2 II). These phases were found to be isostructural with 4H(b)- TaSe_2 (Brown and Beerntsen, 1965) with the same

Table 1. Synthesis of niobium dichalcogenides at 90 kbar.

Temperature (°C)	Starting materials		
	Nb + 2S	Nb + 2Se	Nb + 2Te
<600	no reaction	no reaction	no reaction
600–800	mixture of phases 3R-NbS ₂ 3R-NbS ₂ + 2H-NbS ₂ NbS ₂ II	NbSe ₄ ^a + Nb 2H-NbSe ₂ NbSe ₂ II	NbTe ₄ ^b + Nb NbTe ₄ + Nb ₅ Te ₄
800–1000			
1000–1200			
1200–1350			

^a β -NbSe₄ (Selte and Kjekshus, 1965).

^b High pressure phase NbTe₄ II (Bjerkelund *et al.*, 1968).

Table 2. Interatomic distances (Å) for the new polymorphs of niobium dichalcogenides.

	Nb-X (trigonal-prismatic coordination)	Nb-X (octahedral coordination)	X-X (between layers)
NbS ₂ II	2.48	2.47	3.42
NbSe ₂ II	2.58	2.57	3.56