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NMR INVESTIGATIONS IN SOME COMPOUNDS OF Cr-Te SYSTEM

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The NMR investigations in polycrystalline samples CrTe, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3 are presented. Applying a spin echo technique, two resonance lines are observed in CrTe, Cr_5Te_6, Cr_3Te_4. For Cr_2Te_3 the NMR signal is not observed. The temperature dependence of resonance frequencies was investigated. For Cr_3Te_4 the anomalous behaviour of resonance frequency was found. Additionally, the influence of the heat treatment on the sample properties was studied. Experimental results are discussed in the context of the literature data.

1. Introduction

In this paper we present the results of NMR investigations in some compounds of Cr—Te system. The following polycrystalline samples have been measured: CrTe, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3. These compounds crystallize in a NiAs structure. With less chromium, metal vacancies are formed. This phase can be described as $Cr_{1-x}\square_xTe$. From the neutron diffraction measurements [1] it appears, that the vacancies are placed in every second metal layer. Depending on the parameters of technological process the vacancies can be distributed randomly or form an ordered structure.

It has been shown by several authors as Chevreton et al. [2], Bertaut [2], discussion in [8], Kieu Van Con et al. [3] that stoichiometric compound CrTe does not exist and the correct formula is $Cr_{1-\varepsilon}Te$ (the smallest figure for ε is about 2 atomic percent). The phase $Cr_{1-\varepsilon}Te$ is associated with precipitation of some chromium ions, and the defect of chromium lattice depends on the quenching temperature.

Cr—Te compounds are magnetically ordered, and the temperature of magnetic ordering is, respectively:

CrTe	$T_c = 342 \pm 2$ K	[4],
Cr_5Te_6	$T_c = 327 \pm 2$ K	[1],
Cr_3Te_4	$T_c = 325 \pm 2$ K	[1],
Cr_2Te_3	$T_c = 182 \pm 2$ K	[1].

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The magnetic structure of these compounds is quite complicated and depends on the composition [1, 9]. At certain temperatures, laying in the ferromagnetic region a rapid change of magnetic properties was observed for some of $Cr_{1-x}Te$ compounds. This change was connected with the appearance of antiferromagnetic component in the plane perpendicular to the axis of easy magnetization. This kind of phase transition was observed for Cr_5Te_6 by neutron diffraction [1], for Cr_3Te_4 by neutron diffraction [1] as well as by NMR investigations and magnetization measurements [5, 6]. For CrTe it was observed by magnetization investigations [7].

The purpose of this work were the more complete NMR investigations, including Cr_5Te_6 and Cr_2Te_3 which were not investigated yet by this method and the study of the heat treatment influence on the NMR frequencies as well as the temperature of phase transition.

2. *Experimental*

Sample preparation: the appropriate amounts of Cr and Te (five nine purity), corresponding to CrTe, Cr_5Te_6, Cr_3Te_4, Cr_2Te_3 composition, were sealed in a silica tube at pressure 10^{-5} mm Hg and heated at 1000°C for one week. After that they were cooled with furnace down to the room temperature, ground and again annealed at the same conditions. The equilibrium conditions were tested by *X*-ray examination using Ni-filtered CuK-radiation.

By the spin echo method, two NMR lines were observed in CrTe, Cr_5Te_6, Cr_3Te_4. In Cr_2Te_3 the NMR signal was not observed.

After the first series of measurements, the samples were annealed in two steps at 800°C and 500°C each step lasting one week. Then they were cooled with furnace down to the room temperature.

In the Table I there are presented NMR frequencies observed at 77 K before and after the heat treatment, respectively. In the case of Cr_5Te_6 and Cr_3Te_4 both lines shift towards the lower frequencies after the heat treatment. For CrTe the situation is more

TABLE I

NMR frequencies and corresponding local fields at 77 K. The experimental error is about 0.5 MHz

Sample	Before heat treatment		After heat treatment		Δf_1 (MHz)	Δf_2 (MHz)
	f_1 (MHz)	f_2 (MHz)	f_1 (MHz)	f_2 (MHz)		
	H_{loc} (kOe)	H_{loc} (kOe)	H_{loc} (kOe)	H_{loc} (kOe)		
CrTe	43.5	53.6	41.5	55.2	−2.0	+1.6
	180	222	172	229		
Cr_5Te_6	42.9	53.2	41.0	53.0	−1.9	−0.2
	178	221	170	220		
Cr_3Te_4	41.8	54.0	36.5	47.0	−5.3	−7.0
	173	224	151	195		

complicated, because two NMR lines show frequency shift in the opposite directions. The exceptionally big frequency shift for Cr_3Te_4 compound at 77 K results from the fact that before heat treatment the temperature of phase transition is above the liquid nitrogen temperature and in the annealed sample it is below 77 K. In order to compare the results we give also the NMR frequencies at 4.2 K for this compound (Table II).

TABLE II

NMR frequencies and corresponding local fields for Cr_3Te_4 at 4.2 K

Sample	Before heat treatment		After heat treatment		Δf_1 (MHz)	Δf_2 (MHz)
	f_1 (MHz)	f_2 (MHz)	f_1 (MHz)	f_2 (MHz)		
	H_{loc} (kOe)	H_{loc} (kOe)	H_{loc} (kOe)	H_{loc} (kOe)		
Cr_3Te_4	45.3 188	57.0 237	44.5 185	56.0 233	−0.8	−1.0

The signal intensities for CrTe and Cr_5Te_6 were comparable, both lines being weak and broad. In the case of Cr_3Te_4 the lower line is narrow and intensive, the higher one is weaker and very broad (Fig. 1). It was difficult to find any correlation between the ratio of line intensities and the content of Cr^{3+} and Cr^{2+} or Cr^{2+} and Te^{2-} ions.

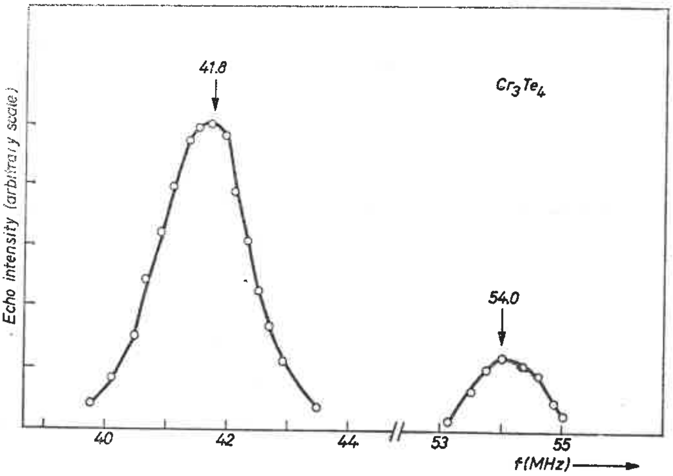

Fig. 1. Spin echo spectrum of Cr^{53} in Cr_3Te_4 at 77 K

The resonance frequencies were investigated as a function of temperature. The results are presented in Fig. 2—5. For Cr_3Te_4 the rapid increase of resonance frequency is observed in the range 80—84 K (Fig. 2). After the heat treatment this transition is observed at 70−75 K (Fig. 3).

In our case the NMR frequencies for Cr_5Te_6 (Fig. 4) and CrTe (Fig. 5) did not show any rapid change with the temperature.

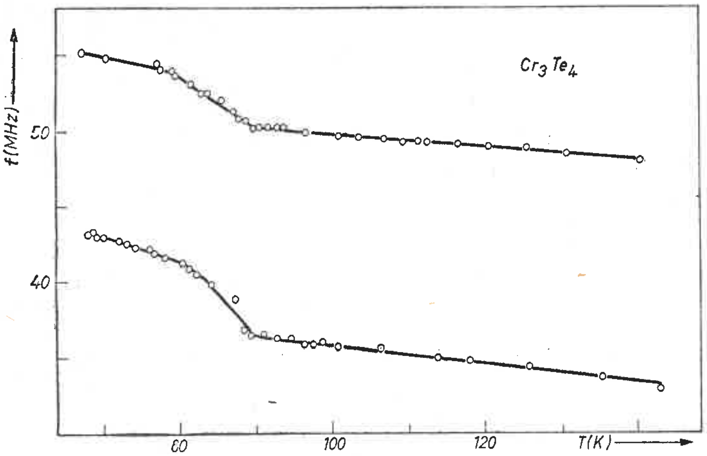

Fig. 2. Temperature dependence of NMR frequency for Cr_3Te_4 before heat treatment

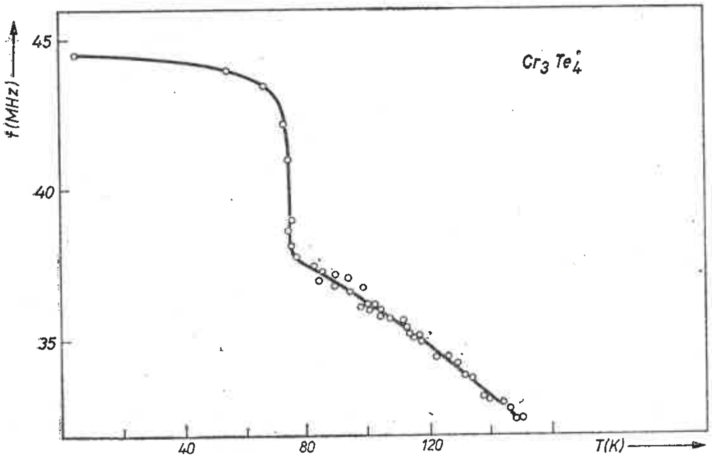

Fig. 3. Temperature dependence of NMR frequency for Cr_3Te_4 after heat treatment

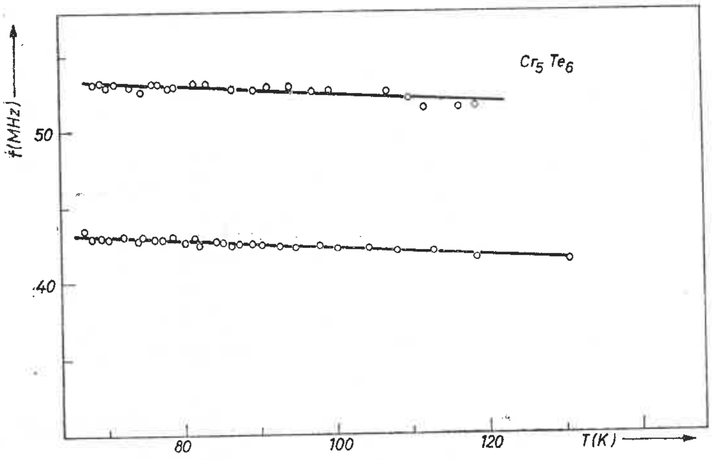

Fig. 4. Temperature dependence of NMR frequency for Cr_5Te_6

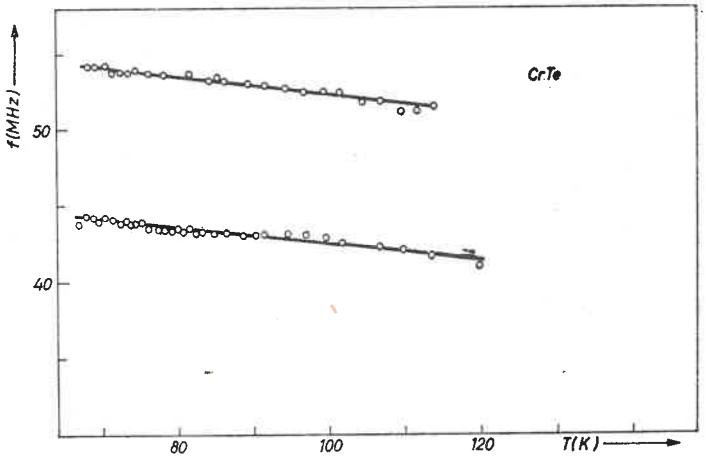

Fig. 5. Temperature dependence of NMR frequency for CrTe

Both NMR signals disappear soon after the application of magnetic field. In the field 4 kGs they were not observed any more. We can thus presume that the signal originates from the domain walls.

3. *Discussion*

As there was no correlation between the content of Cr^{2+}, Cr^{3+}, Te^{2-} ions and the NMR signal intensities, we regard both NMR lines as arising from Cr^{53} nuclei in different sities in accordance with Yamaguchi and Hashimoto [5] who made the same assumption on the basis of their NMR measurements in magnetic field.

The interesting fact is no NMR signal for Cr_2Te_3. This compound shows the characteristic difference of properties, when compared with other compounds of Cr—Te system. One can easily notice the big difference of ordering temperature for this content. This is connected with the ordering of vacancies and weak exchange between the metal layers.

According to Suchet [9], discussion in [8], the nature of magnetic interactions for this content leads to the partially compensated antiferromagnetism. Such a change of magnetic structure would influence the possibility of NMR observation as the amplitude of NMR signal depends strongly on magnetization.

At examining the samples as a function of temperature, we succeeded to observe the phase transition only for Cr_3Te_4 sample. In CrTe and Cr_5Te_6 we did not have this effect, although it was observed in these compounds by other methods (in [7] for CrTe, and in [1] for Cr_5Te_6). On the other hand, in NMR studies Le Dang Khoi [6] neither has seen the phase transition for CrTe, although he observed it for Cr_3Te_4. It is difficult to find the theoretical explanation of this fact and the information of Galkin [7] may be here of some assistance. He found that some of magnetic properties which he observed for single crystal of CrTe did not appear any more in polycrystalline samples.

Our observations of anomalous behaviour of Cr_3Te_4 resonance frequency with the temperature coincide with the NMR and magnetization measurements described by

Yamaguchi et al. [5]. The theoretical explanation of the analogical magnetization changes with the temperature was given for CrTe by Galkin [7]. On the basis of energy considerations, he introduces the model describing the transition from the collinear ferromagnet to the non-collinear spin arrangement, induced by the orthorhombic deformation of the crystal lattice at lowering the temperature. As a result of this process the antiferromagnetic component appears in the plane perpendicular to the easy axis below certain temperature.

The same mechanism can properly describe the phase transition in Cr_3Te_4 observed by us in NMR investigations.

Lower temperature of phase transition for the sample after thermal treatment confirms the above model. One can expect that the more ordered structure, formed during the thermal treatment is less likely to deform, lowering the temperature of additional magnetic moment appearance.

In this way our investigations show the important influence of heat treatment on the magnetic properties of Cr—Te compounds. This fact can be the ground for explanation the diversity of many properties of these materials.

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REFERENCES

[1] A. F. Andresen, *Acta Chem. Scand.* **24**, 3495 (1970).
[2] M. Chevreton, E. F. Bertaut, F. Jellinek, *Acta Cryst.* **16**, 431 (1963).
[3] Kieu Van Con, J. Suchet, *C. R. Acad. Sci.* **256**, 2823 (1963).
[4] A. Ohsawa, Y. Yamaguchi, N. Kazama, H. Yamauchi, H. Watanabe, *J. Phys. Soc. Jap.* **33**, 1303 (1972).
[5] M. Yamaguchi, T. Hashimoto, *J. Phys. Soc. Jap.* **32**, 635 (1972).
[6] Le Dang Khoi, P. Veillet, *C. R. Acad. Sci.* **264B**, 1154 (1967).
[7] A. A. Galkin, E. A. Zawadzki, V. Ya. Sinelnikov, *Ukr. Fiz. Zh.* **19**, 834 (1974).
[8] D. E. Cox, G. Shirane, W. J. Takei, Proc. Int. Conf. on Magnetism, Nottingham 1964, p. 291.
[9] J. Suchet, *C. R. Acad. Sci.* **257**, 1756 (1963).