Abstract. \(	ext{Cr}_2\text{Te}_3\) bulk samples were obtained by melting powdered \(	ext{Cr}_2\text{Te}_3\) at high temperatures (1300-1340 °C). Electron paramagnetic resonance experiments were carried out in an X-band (9.4 GHz) spectrometer in the 150–300K temperature range. There was a great difference between the EPR results of the bulk alloy samples and those obtained for the parent compound, powdered \(	ext{Cr}_2\text{Te}_3\). The transition to the ferromagnetic phase was determined at 212K. Another temperature value of a magnetic phase transition was observed near the room temperature, as well.

1. INTRODUCTION

Chromium chalcogenides may be materials for producing spintronic devices used alternatively to diluted magnetic semiconductors. Cr-chalcogenides reveal a hexagonal crystal structure of the AsNi-type (Fig. 1). Crystals of this type have attracted considerable attention due to their layered structure that determines peculiar electrical and magnetic properties of such materials (e.g. a new FeAs type of high temperature superconductivity [1,2]). Moreover, the variation of the number or arrangement of Cr–vacancies as well as the substitution of metal ions in Cr-chalcogenides lead to the rise of different classes of crystals of the \(\text{Cr}_{1-x}\)(Te, S, Se) type with a wide range of many fascinating electrical and magnetic properties which depend on the number of Cr vacancies indicated by \(x\). Crystals of these compounds such as \(\text{Cr}_{1-x}\)Te [3] exhibit antiferromagnetism, non-collinear spin structures or itinerant electron magnetism [4]. The substitution of Cr atoms with Ti or V creates new properties such as spin-glass [5,6].

Premelted \(\text{Cd}_{1-x}\)Te for \(x=0.33\) (\(x\) determines the number of Cr vacancies) i.e. \(\text{Cr}_{2-x}\)Te are studied in this paper. The structure of this compound belongs to the trigonal system and is presented in Fig. 1. The Cr vacancies lie in every second metal layer and they are ordered in the vacancy layers as can be seen in Fig. 1 [7,8]. The elementary cell \((a=0.6823\ \text{nm}, \ c=0.1180\ \text{nm})\) is doubled in respect to the \(\text{CrTe}\). The Curie temperature is 170-180K. Theoretical calculations result in the magnetic moment of 3.03 \(\mu_B\) per Cr, whereas neutron diffraction measurements predict ferromagnetic moments of 2.6 \(\mu_B\) for Cr atoms situated in fully occupied layers and it is almost negligible for Cr in vacancy layers [9].

Chromium tellurides are mainly ferromagnetic with metallic conductivity (e.g. \(\text{CrTe}\) is a metal with \(T_c=340K\)). Chromium antimonides, on the contrary, are metallic antiferromagnets with ferromagnetic planes perpendicular to the \(c\) axis \((T_N=710K)\). Chromium sulphides are antiferromagnetic semiconductors like selenides, but the latter reveal metallic conductivity.

Some chalcogenides (such as \(\text{Cr}_{1-x}\)Te or \(\text{Cr}_{1-x}\)Se) exhibit a metastable zinc-blende structure [10] which allows for growth of the zinc-blende solid solution semiconductor compounds with the proper-
ties of diluted magnetic semiconductors, e.g., CrMnTe [11], ZnCrTe [12], ZnCrSe [13]. Recently, Ko and Blamire [14,15] have reported room-temperature ferromagnetism in CrCdTe crystals. In our investigations we have also observed this phenomenon [16]. The origin of such ferromagnetism is not clearly understood yet, and the assumption that it may follow from the Cr$_{1-x}$Te precipitates motivates the aim of the present paper to study the magnetic resonance properties of this compound.

2. EXPERIMENTAL

A CrTe alloy was prepared by melting powdered Cr$_2$Te$_3$ (Alfa Aesar, 99.5%) in an evacuated quartz ampoule at the temperatures of 1300, 1320, and 1340 °C. These particular melting temperatures were chosen because such temperatures were considerably higher than those used in the interdiffusion method of the synthesis of various phases of the Cr-Te system which were in the range of 1100 – 1200 °C [17]. Those higher temperatures seemed to be more advantageous in the synthesis of the three component solid solutions obtained from the melt, based on Cr-chalcogenides and, e.g., Cd-chalcogenides CdTe-CrTe. The melting temperatures proposed by us did not lead to a decomposition of the materials but facilitated homogeneity of the final product. The times of heating and cooling are listed in Table 1. The ingots show a porosity, brittle structure consisting of fine grains. The structure of the samples was examined with optical and scanning electron microscopy.

The EPR spectra were recorded using an X-band (9.4 GHz) spectrometer provided with a gas nitrogen cryostat (Oxford Instrument) with a nominally stabilizing temperature of the sample in the range of 77–500K. The measurements were taken in the temperature range of 150-350K.
135

**Table 1.** The Cr$_{1-x}$Te alloy samples prepared for this study.

<table>
<thead>
<tr>
<th>sample</th>
<th>crystal</th>
<th>melting temp. [°C]</th>
<th>melting time</th>
<th>cooling time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cr$_{1-x}$Te</td>
<td>1300</td>
<td>1 h</td>
<td>3 h 15 min</td>
</tr>
<tr>
<td>2</td>
<td>Cr$_{1-x}$Te</td>
<td>1320</td>
<td>1 h</td>
<td>3 h 45 min</td>
</tr>
<tr>
<td>3</td>
<td>Cr$_{1-x}$Te</td>
<td>1340</td>
<td>30 min</td>
<td>4 h</td>
</tr>
<tr>
<td>4</td>
<td>Cr$_2$Te$_3$ powder</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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3. RESULTS AND DISCUSSION

The temperature dependence of the EPR spectrum of sample No. 1 is shown in Fig. 2.

As can be seen in Fig. 2, the shape of the EPR line depends strongly on the temperature. In the vicinity of the room temperature the lines become very broad and weak or disappear completely. At lower temperatures the shape of the lines approaches the Lorentz function. The asymmetry of the lines is also visible which can be attributed to the strong exchange interactions as well as to the semimetal electrical conductivity. The shape of the spectra is characteristic for a paramagnetic phase above room temperature.

We extracted the parameters of the lines: intensity $I$, resonance field $H_r$, and width $H_{pp}$ from the fitting of the theoretical Lorentz formulae to the experimental spectra at each temperature. Many lines were shifted significantly to the small resonance fields which resulted in partial detection of the resonance signal derivative. In such case it was possible to fit the recorded part of the line with the Lorentz behaviour as well. In Fig. 3 the fits of the experimental EPR line to the Lorentz function are presented as an example.

Fig. 4 shows the linewidth and the $g$ factor dependence on temperature for samples Nos. 1, 2, and 3. Above room temperature the lines are stable with regard to both their position and width, and they are relatively narrow. Two temperature ranges can be seen in Fig. 4 where the linewidth increases drastically and the line disappears absolutely. This takes place for the temperature range of 280–300K and below 220K.

The calculated $g$ factor at the room temperature has the value of 1.98. The factor changes moder-
ately below the room temperature due to the rise of an internal field. This change is however quite significant below 220K.

In Fig. 5, we have compared the spectra of $\text{Cr}_2\text{Te}_3$ alloys (samples Nos. 1, 2, 3) with those obtained for the powdered $\text{Cr}_2\text{Te}_3$ (sample No. 4) which was the parent material for the preparation of alloy samples. These spectra were recorded at room temperature. As can be observed, there is a great difference between the spectra of the latter sample and those of the former ones.

Comparing the EPR spectra for samples Nos. 1, 2, 3 it can be concluded that the technological parameters applied in the present study influence strongly neither the EPR spectrum line width nor the discontinuity position of temperature dependencies in the diagrams. However, there is a strong dependency of the line position (g factor) on the melting temperature. The difference is especially visible for EPR measurements at low temperatures (see Fig. 4b).

The EPR spectra of sample No 2 exhibit non-ordinary features. Below 290K, the spectra consist of two lines as can be seen in Fig. 6. The dominated line moves towards low magnetic resonance fields with the decreasing temperature, whereas the second line is going in the opposite direction. Both components are relatively wide, and the second line is of a much smaller intensity. The large broadening of the investigated lines is a result of the great interaction between magnetic moments. On the other hand, the EPR line splitting into two components in the case of sample No. 2 at lower temperatures can be attributed to a great magnetic anisotropy in the ferromagnetic phase. The samples reveal a crystal structure with a prevailing axial symmetry [10], giving two g factor values: $g_\parallel$ and $g_\perp$. In polycrystalline samples, all spins are statistically randomly oriented. Therefore, it may be expected to observe the EPR spectrum spreading over the $\Delta B$ field range determined by the g tensor. However, the lines are not uniformly distributed over this magnetic field range. Thus, the great magnetic anisotropy for polycrystalline samples results in the rise of two lines in the EPR experiment [18]. The effect is enhanced considerably in the ferromagnetic state. The temperature dependence of the positions of these two lines of sample 2 is presented in Fig. 7 as a shift $H_r(T) - H_r(240K)$ of the line positioning from the high temperature limit $H_r(240K)$. Such behavior is intrinsic to the layered magnetic systems with two-dimensional ferromagnetic fluctuations above the Curie temperatures. It has been also observed in layered perovskite manganites (see e.g. [19]).

The inset in Fig. 4a shows the least-square fit of Huber’s [20] expression: to a part of the $\Delta H_{pp}(T)$ data

$$\Delta H_{pp} = A\left(\frac{T_c}{T - T_c}\right)^\alpha + B,$$

(1)
where $\alpha$ is a critical exponent, $B$ is the temperature-independent linewidth, $T_c$ is the order-disorder transition temperature, $A$ is a constant.

The value of $T_c$ determined from Eq. (1) is found to be $T_c = 212K$ at $\alpha = 1.1$ and $B = 95$ mT. This value is identified with the Curie temperature as the $\alpha$ is close to the value of 1. Thus, the Huber’s equation approximates the Curie–Weiss law. So far, a number of Cr$_x$Te compounds have $T_c$ ranging from 170K to 360K depending on the number $x$ of Cr vacancies (Table 2). The value of $T_c$ obtained in our paper does not match any of those listed in Table 2, even this for the parent compound Cr$_2$Te$_3$. The difference could be due to the clustering of chromium atoms in the layers, which results in a decrease in $x$ and enhanced $T_c$.

In Fig. 8 we have collected the integrated intensity $I_{EPR}$ for all the three samples calculated as:

$$I_{EPR} = l\left(\Delta H_{pp}\right)^2,$$

where $l$ is the amplitude of the EPR absorption field derivative.

The anomaly in the temperature dependence of the EPR linewidth and the integrated intensity observed at room temperature in Fig. 4 and in Fig. 8 could be attributed to low–dimensional ferromagnetic effects. Such low–dimensional ferromagnetic fluc-
tations may follow a high-temperature magnetic transition. Chauvet et al. [24] observed the magnetic transition at 350K above the Curie temperature $T_c = 110K$ in the layered manganites $\text{La}_{1.35}\text{Sr}_{1.65}\text{Mn}_2\text{O}_7$. Moreno et al. [19] investigated also manganites $\text{La}_{1.35}\text{Sr}_{1.65}\text{Mn}_2\text{O}_7$ and $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ by EPR and observed additional transitions for $T \sim 450-500K$ also well above $T_c$. The linewidth anisotropy and the spectrum splitting into two lines with the decreasing temperature were addressed as intrinsic features of the layer systems. Recently, two-dimensional spin fluctuations in layer crystals $\text{GdI}_2$ have been studied by EPR by Deisenhofer [25]. The experimental results have been described by a two-dimensional Heisenberg ferromagnet model proposed by Eremin et al. [26]. The structure of $\text{GdI}_2$ is similar to that of chromium chalcogenides. There are hexagonal planes of magnetic ions. These planes are separated by planes of nonmagnetic I ions. The high-temperature two-dimensional ferromagnetic transition in $\text{GdI}_2$ was observed at $T_c = 276K$ [25].

In Fig. 8 the theoretical dependence $\chi(T)$ given by Deisenhofer [25] has been plotted (as a solid line):

$$\chi_{\text{spin}}(T) \propto -\frac{16\sqrt{3} S^2 J_{||}}{T} - \frac{J_\perp}{6\sqrt{3} S J_{||}}$$

for $S=3/2$, $J_{||} = 57$, $J_\perp = 0.006$, and $A = 1.4*10^{-6}$.

Here $J_{||}$ and $J_\perp$ are ferromagnetic exchange constants within and inter the Cr layers, respectively, $A$
Table 2. Curie temperatures for Cr$_{1-x}$Te compounds.

<table>
<thead>
<tr>
<th>Cr$_{1-x}$Te</th>
<th>CrTe</th>
<th>Cr$<em>{23}$Te$</em>{24}$</th>
<th>Cr$<em>{7}$Te$</em>{8}$</th>
<th>Cr$<em>{8}$Te$</em>{6}$</th>
<th>Cr$<em>{6}$Te$</em>{4}$</th>
<th>Cr$<em>{2}$Te$</em>{3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$</td>
<td>0</td>
<td>0.042</td>
<td>0.125</td>
<td>0.167</td>
<td>0.25 [4]</td>
<td>0.33</td>
</tr>
<tr>
<td></td>
<td>343K [21]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>342K [22]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>350K [23]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

is the proportionality coefficient. It can be noticed that the agreement of the theoretical dependence with the experimental data, particularly in a high temperature regime, is not very good. Nevertheless, these dependence estimates adequately the Curie temperature of the two-dimensional ferromagnetic fluctuations addressed by us. However, at this stage of the study the supposition that this high-$T$ mag-
netic anisotropic effects resulting in the EPR line
but follows from the second phase cannot be rigor-
ously rejected. Such discrepancies in the interpre-
tation of the data exist in literature (see e.g. Moreno
et al. [19] and the references therein).

4. CONCLUSIONS

The crystal structure of Cr$_2$Te$_3$ gives grounds to as-
sert that the magnetism in the plane perpendicular
to c axis is two-dimensional. The g factor and the
linewidth dependence on temperature indicates the
presence of two temperatures at which magnetic
transitions are observed. The first transition, around
300K, can be assumed to be a result of two-dimen-
sional ferromagnetic correlated Cr clusters in the a-
b plane. The second transition, at 212K, is attrib-
uted to the phase transition of bulk ferromagnetism.
The measurements of sample 2 (heating tempera-
ture 1320 °C) show the presence of strong mag-
netic anisotropic effects resulting in the EPR line
splitting above the Curie temperature.

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