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## Resistance, magnetic susceptibility in (T, Nb)Nb<sub>2</sub>Se<sub>10</sub> with T = Fe, Cr (+)

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**Résumé.** — Nous avons préparé Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> (avec  $x = 0,32, 0,38$ ) et Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub>. Les composés, placés sous vide en tubes de silice scellés, ont été chauffés à 750 °C. La détermination structurale a été effectuée par la méthode de Weissenberg. La transition métal-isolant de Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> et de Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub> a été étudiée par des mesures de résistivité et de susceptibilité magnétique. La transition métal-isolant est associée avec les ondes de densité de charge dans les chaînes NbSe<sub>3</sub>, ce qui donne une transition métal-isolant de type Anderson. La transition métal-isolant de Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> apparaît à 140 K et croît jusqu'à 190 K pour Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub>.

**Abstract.** — Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> with  $x = 0.32, 0.38$  and Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub> were prepared by heating in evacuated silica tubes. The structure was determined by Weissenberg photograph. The metal-insulator transition of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> and of Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub> was studied by measurements of resistivity, and magnetic susceptibility. The metal-insulator transition is correlated with the CDW which depresses the conductivity in the NbSe<sub>3</sub>-chains and gives an Anderson type metal-insulator transition. The metal-insulator transition of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> appears at 140 K and increases to 190 K for Cr<sub>1,45</sub>Nb<sub>2,55</sub>Se<sub>10</sub>.

### 1. Introduction.

Niobium triselenide has a crystal structure consisting of face-sharing NbSe<sub>6</sub> triangular prisms [1] and exhibits two incommensurate charge density waves (CDW's) with onset temperatures of 144 and 59 K [2]. The NbSe<sub>6</sub> trigonal prisms form infinite chains of three types running parallel to the monoclinic *b* axis with metal-metal pairs along the chains [3]. The non-linear conductivity of this compound is thought to originate from a sliding-mode CDW. This can be depinned from impurities in the lattice by application of a small electrical field. It is generally observed that CDW's are suppressed by sufficient doping with foreign atoms [4]. A modest substitution of niobium by Ta [5], Ti [6], Co or Mo [7] results in a stronger pinning of the CDW to the lattice.

Hillenius *et al.* [8] have prepared a compound Fe<sub>0.25</sub>Nb<sub>0.75</sub>Se<sub>3</sub>, but this compound has the nominal composition FeNb<sub>3</sub>Se<sub>10</sub>. Its resistivity increases by nine orders of magnitude between 140 and 3 K; this increase is supposed to originate from the atomic disorder due to Anderson localization.

X-ray scattering showed the CDW to be incommensurate, with a *q* of (0.0; 0.27; 0.0) at onset and the CDW wave vector is only slightly different from the high-temperature CDW in NbSe<sub>3</sub>, where *q* = (0.0, 0.24, 0.0) with an onset of 144 K. In Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> a large amount of Fe  $0.25 < x < 0.4$  can be incorporated without quenching the CDW. A. Ben Salem *et al.* [9] investigated compounds with the composition (Fe, V)Nb<sub>2</sub>Se<sub>10</sub> and Cr<sub>2</sub>Nb<sub>2</sub>Se<sub>10</sub> with changing of the metal atoms in the octahedral chain.

The present study shows the influence of the Fe content in FeNb<sub>3</sub>Se<sub>10</sub> on the electrical conductivity and the magnetic susceptibility. A substitution of Fe by Cr was also investigated. FeNb<sub>3</sub>Se<sub>10</sub> and

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$\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  are composed of two  $\text{NbSe}_6$  trigonal prismatic chains and a double chain of the edge-shared  $\text{FeSe}_6\text{NbSe}_6$  or  $\text{CrSe}_6\text{NbSe}_6$  and  $\text{FeSe}_6\text{FeSe}_6$  or  $\text{CrSe}_6\text{CrSe}_6$  octahedra. Only in the case of the octahedral chain the metal atom disorder explains the relatively small perturbation of the CDW which is likely to occur in pure  $\text{NbSe}_3$  [10, 11].

## 2. Experimental.

$\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  and  $\text{Cr}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  single crystals were prepared by mixing the desired amounts of powders of the elements (Fe 99.99% Goodfellow Metals, Nb m4N Ventron GmbH Puratronic, Cr 99.5% Pierce Eurochemie B.V., and Se 99.999% Koch-Light Laboratories Ltd) which were sealed in high evacuated quartz tubes (at  $1.4 \times 10^{-4}$  Pa). A small temperature gradient at 700 °C was maintained for about three weeks and then the samples were quenched in cold water. Needlelike dark metallic crystals which looked similar to pure  $\text{NbSe}_3$  grew in the quartz tubes both in the case of  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  and  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$ . The colour of  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  is silver metallic. The single crystal needles are  $\sim 12$  mm long and  $\sim 0.4$  mm broad. The stoichiometry of the crystal specimens was analysed by the use of a X-ray microprobe. The results gave the chemical composition  $\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$  and  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$ .

Weissenberg photographs showed that in case of both compounds the symmetry was monoclinic with the space groups  $\text{P}2_1$  or  $\text{P}2_1/m$ . The lattice parameters have been determined by rotation and Weissenberg photographs. The reduced cell was refined from X-ray powder data using least square techniques.

The powder data are given in table I. Si(NBS  $a = 5,430752 \text{ \AA}$ ) was used as standard material. The intensities of reflections are influenced by texture effects.

$\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$	$\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$
$a = 9.218(1) \text{ \AA}$	$a = 9.207(2) \text{ \AA}$
$b = 3.498(1) \text{ \AA}$	$b = 3.544(1) \text{ \AA}$
$c = 10.282(2) \text{ \AA}$	$c = 10.428(2) \text{ \AA}$
$\beta = 114.42(2)^\circ$	$\beta = 115.45(2)^\circ$

The lattice parameters of the  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  compounds are in good agreement with the data of Cava *et al.* [12]. In the case of the substitution of Fe by Cr the lattice constants  $b$  and  $c$  increase considerably, whereas the lattice parameter  $a$  exhibits a small decrease.

The magnetic susceptibility was determined with the susceptibility apparatus SUS 10 (manufactured by A. Paar KG Graz, Austria) that is based upon the Faraday method using a sensitive pendulum system. The device guarantees complete indifference against torques in the magnetic fields. KCl (« suprapur » quality, E. Merck, Darmstadt) was used as calibration compound because only diamagnetic and/or small paramagnetic effects had to be investigated. Data were collected at external magnetic fields of 4.1, 7.1, 9.9,

Table I. — *Index of powder diffraction for  $\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$  and  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$ .*

$h k l$	$\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$			$\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$		
	$I/I_0$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I/I_0$	$d_{\text{obs}}$	$d_{\text{calc}}$
0 0 $\bar{1}$				5	9.482	9.416
1 0 0	70	8.393	8.394	30	8.371	8.313
1 0 $\bar{1}$	5	8.184	8.143			
1 0 1	70	5.261	5.262	65	5.240	5.218
1 0 $\bar{2}$	15	5.082	5.078			
2 0 $\bar{1}$	25	4.601	4.606	15	4.618	4.603
2 0 0	15	4.193	4.197	15	4.164	4.157
0 1 $\bar{1}$				5	3.314	3.317
0 0 3				70	3.142	3.139
3 0 $\bar{1}$	30	3.046	3.049	30	3.034	3.035
3 0 $\bar{2}$	30	3.010	3.012	20	3.025	3.022
3 0 0	10	2.796	2.798			
3 0 $\bar{3}$	20	2.713	2.714	10	2.743	2.743
2 0 2	20	2.630	2.631	20	2.608	2.609
1 0 3	15	2.597	2.596	20	2.594	2.591
1 0 $\bar{4}$	40	2.544	2.543	50	2.574	2.573
2 1 1	20	2.419	2.418			
0 0 4				10	2.352	2.354
3 1 $\bar{1}$				30	2.305	2.305
1 1 3				100	2.091	2.092
4 0 0	60	2.099	2.098	30	2.078	2.078
1 1 $\bar{4}$	20	2.056	2.057			
3 0 $\bar{5}$	5	1.980	1.980	10	2.009	2.010
5 0 $\bar{2}$	10	1.841	1.840	10	1.834	1.835
5 0 $\bar{1}$	100	1.786	1.786			
0 2 0	15	1.749	1.749	50	1.772	1.772
5 0 $\bar{5}$				10	1.646	1.646
0 0 6				60	1.569	1.569
5 0 1	25	1.545	1.545			

and 12.1 kOe in the temperature range between 77 and 550 K. The susceptibility values had to be corrected for the diamagnetic contribution of the atoms [13, 14]. For anisotropic measurements single crystals ( $\sim 4$  mm long and  $\sim 0.4$  mm broad) were mounted on a special sample holder which can be turned by a micrometer in steps as small as 0.1 degree. The measurements were calibrated by a piece of pure tungsten or nickel of similar size and shape as the crystals.

## 3. Results and discussion.

The temperature dependence of the resistivity of  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  is compounds with  $x = 0.32, 0.38$  and  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  shown in figure 1. Below 100 K a strong increase of the resistivity was found for all samples.  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  has a minimum of resistivity at 190 K. Above this temperature an increase of resistivity was observed again.

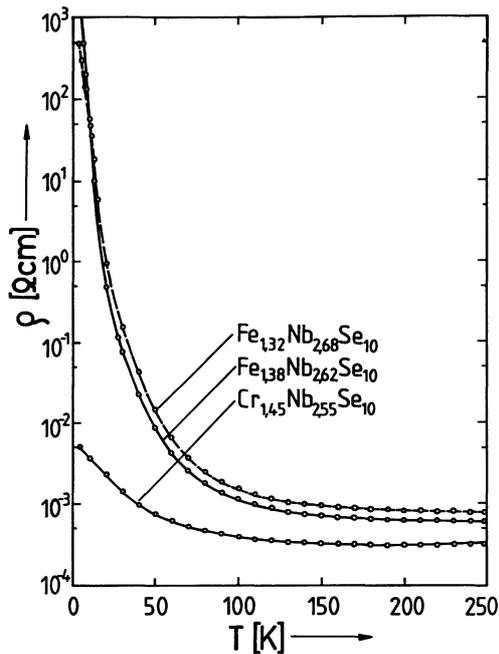


Fig. 1. — Temperature dependence of the resistivity of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> (x = 0.32, 0.38) and of Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub>.

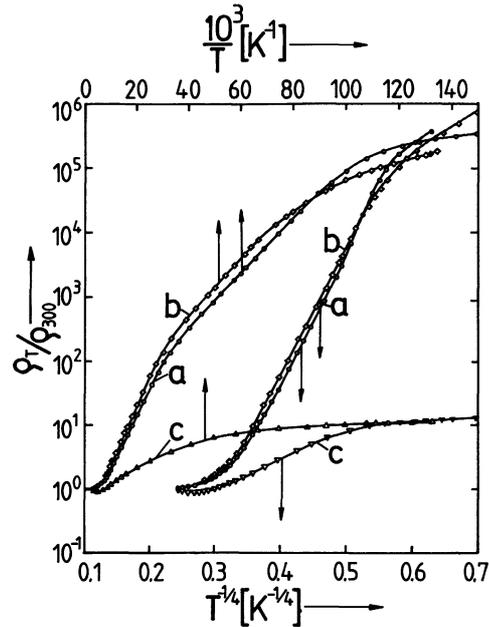


Fig. 2. — Resistivity relation  $\rho_T/\rho_{300}$  of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> (x = 0.32; 0.38) and of Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> vs.  $T^{-1}$  (upper scale) and  $T^{-1/4}$  (lower scale) between 300 and 4.2 K. a) Fe<sub>1.38</sub>Nb<sub>2.62</sub>Se<sub>10</sub>, b) Fe<sub>1.32</sub>Nb<sub>2.68</sub>Se<sub>10</sub>, c) Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub>.

Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub>

The temperature dependence of the electrical resistance has been fit for x = 0.32 and 0.38 to various functional relations (see Figs. 2 and 3). We found that no unique expression valid over the entire temperature range exists. The temperature dependence of the electrical resistance of the crystals is similar to that of Hillenius *et al.* [8] for samples with a lower Fe-content.

Above 140 K for all measured Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> samples a very small exponential increases as a function of  $T^{-1}$  was found with decreasing temperature.

The resistivity showed the form

$$\rho = \rho_0 \cdot e^{A/kT} \quad \text{and} \quad \rho = A \cdot e^{(T_0/T)^{1/4}}$$

in the range between 300 and 10 K.

The stronger rise in the resistivity at 120-140 K is correlated with the onset of the weak superlattice observed in the X-ray investigations at 120 K [8, 15]. Two types of diffuse scattering as a function of temperature were found [15]. The satellites of the type 1 [15] correspond to the reduced components along *b* (collinear with *b*, chain axis) and are slightly larger than 1/4. This is in good agreement with Hillenius *et al.*

The spots of type 1 come from the onset of a charge-density wave affecting the trigonal prismatic chains.

The type 2 spots of the diffuse scattering determined by R. Moret *et al.* [15], however, have a reduced *b* component with  $b = 1/3$  and  $q = (0.5, 0.33, 1)$ . The intensity of the type 2 spots is higher than that of the

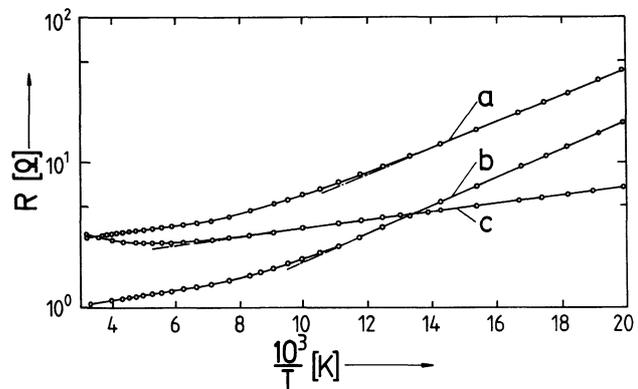


Fig. 3. — Electrical resistance as a function of inverse temperature of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> (x = 0.32; 0.38) and of Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> between 300 and 50 K.

- a) Fe<sub>1.38</sub>Nb<sub>2.62</sub>Se<sub>10</sub>, b) Fe<sub>1.32</sub>Nb<sub>2.68</sub>Se<sub>10</sub>,
- c) Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub>.

type 1. Starting from room temperature the intensity rises slowly up to about 150 K, from that on it increases faster.

The minimum of the magnetic susceptibility of FeNb<sub>3</sub>Se<sub>10</sub> at 190 K corresponds to the appearance of the type 1 spots of the diffuse X-ray scattering (see Fig. 5).

Between 95 and 50 K the temperature dependence of the resistivity can be approximated by a straight-line

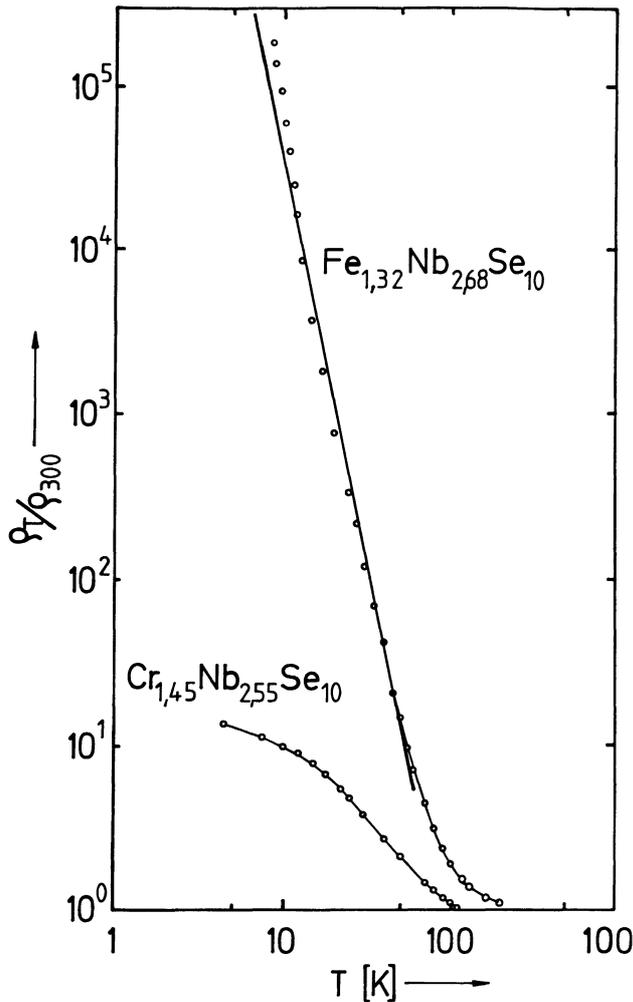


Fig. 4. — Resistivity relation  $\rho_T/\rho_{300}$  versus temperature for  $\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$  and  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  plotted on log scales.

segment with a slope  $\Delta = 0.031$  for  $x = 0.32$  and  $\Delta = 0.035$  for  $x = 0.38$ . This probably indicates the existence of a region with an activated conductivity,  $\rho \propto e^{\Delta/2kT}$ , which may be caused by a charge density wave. Between 10 and 4.2 K we found that the temperature dependence of the resistance is  $\rho \propto e^{(T_0/T)^m}$  with  $m = 0.5$  to 1. In the temperature range between 60 and 20 K also a  $T^{-1/4}$  dependence of the log of resistivity is possible.

A functional dependence of  $\rho \propto T^{-m}$  gives  $m = 5.4$  for  $\text{Fe}_{1.38}\text{Nb}_{2.62}\text{Se}_{10}$  and  $m = 5.0$  for  $\text{Fe}_{1.32}\text{Nb}_{2.78}\text{Se}_{10}$  between 4.2 and 80 K (Fig. 4). This is in agreement with Cava *et al.* It is difficult to decide which relation is the best in this range because the resistivity has a high exponential temperature dependence. S. J. Hillenius and R. V. Coleman [16] suggest that the metal-insulator transition is correlated with the CDW which depresses the conductivity in the Nb-chains and gives an Anderson type metal-insulator transition due to the random potential generated by Fe.

The rise in the resistivity is correlated with the appearance of an incommensurate charge

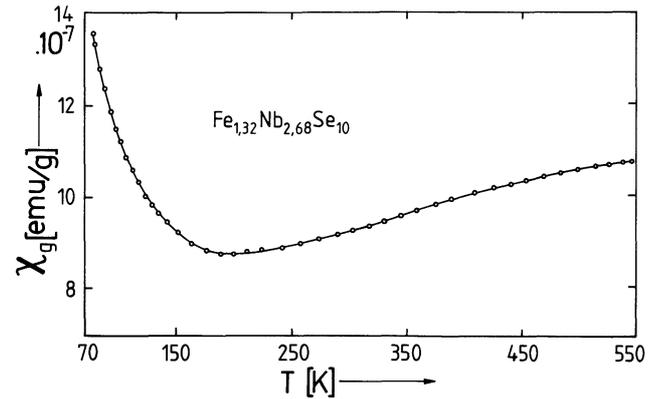


Fig. 5. — Temperature dependence of the magnetic susceptibility for  $\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$  powder.

density wave (CDW). We think that the formation of a gap associated with a CDW may exhibit an activated resistivity below the onset. The CDW in  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  arises from a nearly one-dimensional band based on the Nb-atoms [17]. The value of the resistivity depends on the chemical composition [18] and on the ordered arrangements of Fe- and Nb-atoms in the octahedral chains of  $\text{FeNb}_3\text{Se}_{10}$  at low temperatures. This is confirmed by the increase of the lattice parameters  $a$  and  $c$  with increasing Fe-content in the compounds.

#### $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$

The lattice parameters increase with substitution of Fe by Cr because the distances of the octahedra between the trigonal prismatic chains are changed. This causes the decrease of the resistivity in comparison to  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  and the weaker pinning of the CDW in  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$ . Above 190 K a metallic conductivity with a positive temperature coefficient of resistivity (Fig. 1) is found.

Between 110 and 50 K we also found a  $\rho \propto e^{\Delta/2kT}$  relation with  $\Delta = 0.011$  eV. Between 50 and 20 K the situation is the same as in  $\text{Fe}_{1+x}\text{Nb}_{3-x}\text{Se}_{10}$  and we cannot decide what is the best relation.

Below 10 K the resistivity has a very weak increase. A functional dependence of  $\rho \propto T^{-m}$  gives  $m = 1.12$  between 10 and 100 K (Fig. 4).

#### Magnetic susceptibility.

The temperature dependence of the magnetic susceptibility of  $\text{Fe}_{1.32}\text{Nb}_{2.68}\text{Se}_{10}$  is shown in figure 5.

It exhibits a minimum value at about 180 K and increases with rising temperature up to 500 K. Between 77 and 180 K it increases with decreasing temperature and can be fit to a Curie-Weiss expression  $\chi - \chi_0 = C/(T - \Theta)$ . The value of the susceptibility is a function of the Fe content [17]. The magnetic susceptibility of  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  is also paramagnetic. This is shown for  $\text{Cr}_{1.45}\text{Nb}_{2.55}\text{Se}_{10}$  powders in figure 6. The values of the magnetic susceptibility changes remar-

kably with the crystal direction (Fig. 7 for the direction  $\parallel b$  and  $\perp b, c$  axis). A change in the increase of the susceptibility between 170 and 200 K as a function of the crystal direction has been found. At 180 K, however, Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> shows no minimum of the susceptibility. A more detailed study to the angular dependence of the magnetic susceptibility and to the Mössbauer spectra of the compounds with Fe content is to be published [18].

#### 4. Conclusions.

The lattice parameters of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> increase with increasing Fe content. Fe<sub>1.32</sub>Nb<sub>2.68</sub>Se<sub>10</sub>, however, has a metal-insulator transition at 140 K like FeNb<sub>3</sub>Se<sub>10</sub> investigated by Hillenius *et al.*, but at very low temperature its resistivity is slightly lower. The increased Fe-content does not produce a well remarkable change in the behaviour of the CDW. The magnetic susceptibility of this compound shows a minimum at 180 K caused by the formation of a superlattice.

Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> has larger lattice parameters and a metal-insulator transition, too. At low temperatures the resistivity is remarkably lower than in Fe<sub>1.32</sub>Nb<sub>2.68</sub>Se<sub>10</sub>.

At 190 K a minimum of the resistivity and a change in the increase of the magnetic susceptibility were found. This is supposed to be caused by an appearance of a charge-density wave at this temperature and increased atom distances between the two trigonal prismatic niobium chains opposite to the atom distances of Fe<sub>1+x</sub>Nb<sub>3-x</sub>Se<sub>10</sub> compounds.

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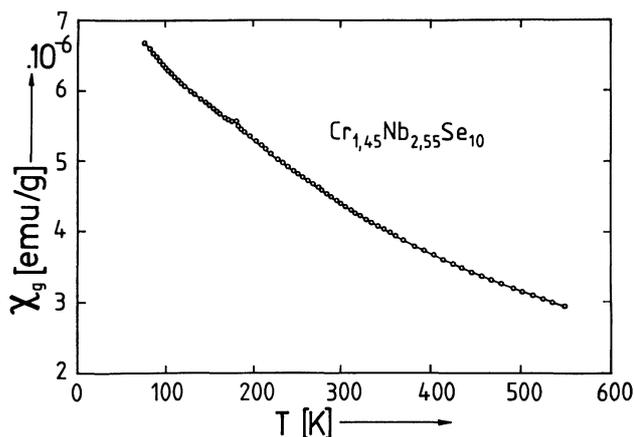


Fig. 6. — Temperature dependence of the magnetic susceptibility for Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> powder.

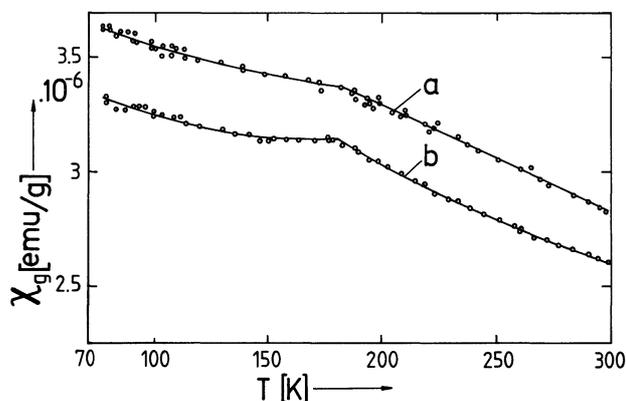


Fig. 7. — Temperature dependence of the magnetic susceptibility for Cr<sub>1.45</sub>Nb<sub>2.55</sub>Se<sub>10</sub> crystals. a) Magnetic field  $\perp b, c$ ; b) Magnetic field  $\parallel b$ .

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#### References

- [1] HODEAU, J. L., MARENZIO, M., ROUCAU, C., AYRDES, R., MEERSCHAUT, A., ROUXEL, J., MONCEAU, P., *J. Phys. C* **11** (1978) 4117.
- [2] TSUTSUMI, K., TAKAGAKI, T., YAMAMOTO, M., SHIOZAKI, Y., IDO, M., SAMBONGI, T., YAMAYA, K., ABE, Y., *Phys. Rev. Lett.* **39** (1977) 1675.
- [3] RIJNSDORP, J., JELLINEK, F., *J. Solid State Chem.* **25** (1978) 325.
- [4] FLEMING, R. M., GRIMES, C. C., *Phys. Rev. Lett.* **42** (1979) 1423.
- [5] ONG, N. P., BRILL, J. W., ECKERT, J. C., SAVAGE, J. M., KHANNA, S. K., SOMOANO, R. B., *Phys. Rev. Lett.* **42** (1979) 811.
- [6] BRILL, J. W., ONG, N. P., ECKERT, J. C., SAVAGE, J. W., KHANNA, S. K., SOMOANO, R. B., *Phys. Rev. B.* **23** (1981) 1517.

- [7] GRUBER, H. and SASSIK, H., Proceedings Synthetic low dimensional Conductors and Superconductors, *J. Physique Colloq.* **44** (1983) C3-1717.
- [8] HILLENUS, S. J., COLEMAN, R. V., FLEMING, R. M., CAVA, R. J., *Phys. Rev. B* **23** (1981) 1567.
- [9] BEN SALEM, A., MEERSCHAUT, A., GUEMAS, L., ROUXEL, J., SALVA, H., MONCEAU, P., Proceedings Synthetic low dimensional Conductors and Superconductors, *J. Physique Colloq.* **44** (1983) C3-1681.
- [10] MEERSCHAUT, A., GRESSIER, P., GUEMAS, L., ROUXEL, J., *Mat. Res. Bull.* **16** (1981) 1035.
- [11] CAVA, R. J., HIMES, V. L., MIGHELL, A. D., ROTH, R. S., *Phys. Rev. B* **24** (1981) 3634.
- [12] GRUBER, H., KRAUTZ, E., *Phys. Status Solidi (a)* **62** (1980) 615.
- [13] SELWOOD, P. W., *Magnetochemistry*, 2nd ed., 78 (Interscience, New York) 1956.
- [14] WEISS, A. and WITTE, E., *Magnetochemie* (Verlag Chemie, Weinheim) 1973.
- [15] MORET, R., POUGET, J. P., MEERSCHAUT, A., GUEMAS, L., *J. Physique Lett.* **44** (1983) L-93.
- [16] HILLENUS, S. J. and COLEMAN, R. V., *Phys. Rev. B* **25** (1982) 2191.
- [17] WHANGBO, M.-H., CAVA, R. J., DISALVO, F. J., FLEMING, R. M., *Solid State Commun.* **43** (1982) 277.
- [18] GRUBER, H., 2nd Austrian Scientific Exposition Vienna, Austria, Nov. 1981, p. 97. Organizer : Bundeskonferenz des wissenschaftlichen und künstlerischen Personals, 1010 Wien (Ed. : Zentralsparkasse und Kommerzbank, Wien).
- [19] GRUBER, H., FRITZER, H. P., STEINER, W., To be published.
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