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Semiconducting and Magnetic Properties of Rhombohedral Cr_2S_3

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Measurements of the magnetic properties and the electrical resistivity, the Hall effect, the thermoelectric power, and the magnetoresistance were carried out on polycrystalline rhombohedral Cr_2S_3. The electrical transport properties show an anomalous behaviour near the Curie temperature $T_C = 120°K$. These anomalies are ascribed to the interaction between charge carriers and localized magnetic moments, leading to an exchange splitting of the conduction band and to spin-disorder scattering of the charge carriers.

Introduction

Rhombohedral Cr_2S_3 is one of the many compounds occurring in the Cr–S phase diagram (*1–3*). The crystallographic structure, the phase transitions and the magnetic and electrical properties of several of these compounds have been reported previously (*1, 2, 4–6*). The structure of all these compounds can be derived from the NiAs-type structure, by leaving part of the metal sites in every second metal layer unoccupied in an ordered fashion.

Rhombohedral Cr_2S_3 is a ferrimagnet with a Curie temperature of 120°K. Neutron diffraction data (*7*) lead to a collinear spin structure with three magnetic sublattices. Recent magnetization and neutron diffraction data (*8, 9*) show that the spins all lie in a plane perpendicular to the trigonal axis.

The spontaneous magnetization of rhombohedral Cr_2S_3 is very small; it is caused by small differences between the sublattice magnetizations in the nearly antiferromagnetic compound. These differences can be due to a difference in the temperature dependence of the sublattice magnetizations, or to small differences in occupancy by chromium atoms of the various crystallographically different sublattice sites. The magnetization data reported here indicate that both effects are present simultaneously.

The electrical properties of rhombohedral Cr_2S_3 show that the compound is a semiconductor. Both *n*-type (*4*) and *p*-type (*3, 4, 10*) conductivity have been observed, depending on the method of preparation of the samples. The donors and/or acceptors might be due to impurities. However, the existence of various phases in the Cr–S system, and the finite homogeneity region suggest that native defects will play an important role in the chromium sulfides. Excess Cr atoms occupying empty octahedral sites are expected to behave as donor centres, whereas excess Cr vacancies will be acceptors.

In this paper measurements of the magnetic and electrical properties of *n*-type rhombohedral Cr_2S_3 are reported. It will be shown that even the very weak spontaneous magnetization of Cr_2S_3 has a pronounced influence on the electrical transport properties. The electrical data are interpreted in terms of spin-disorder scattering of the charge carriers and exchange splitting of the conduction band.

Experimental Part[1]

Rhombohedral Cr_2S_3 was prepared by direct reaction of the elements during three days at 1000°C. The resulting polycrystalline samples were single-phase and *n*-type conducting. Magnetic measurements were carried out on these powders, using a Faraday balance. For the electrical measurements the powders were pressed for one day with a pressure of 8000 kg/cm² at 330°C in vacuum, followed by annealing in vacuum without pressure during one day at 580°C. The obtained polycrystalline bars were

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[1] More details about the experimental procedures are given in Ref. (*4*).

sintered during one week at 1000°C, followed by slow cooling. In this way densities of more than 90% of the X-ray density were obtained. X-Ray diffraction (using a Guinier camera) showed that only rhombohedral Cr_2S_3 was present after these procedures.

The electrical resistivity, the magnetoresistance and the Hall effect were measured using a dc four-point contact method. The electrical contacts showed good linear characteristics.

The Hall voltage was measured for different values of the magnetic field. The influence of thermal effects on the Hall voltage was eliminated by measuring with various Hall currents. Temperature gradients across the sample were minimized by placing the sample in a massive golden housing. Conventional current- and field-reversal procedures were used to eliminate contributions of other parasitic effects.

Seebeck-effect measurements were carried out in a special sample holder, with a constant thermal gradient across the bar-shaped sample. The sample was situated between two golden spring-loaded pressure-contact blocks.

All electrical measurements were carried out in a nitrogen or helium atmosphere free from oxygen and water vapour.

Magnetic Properties

The magnetic susceptibility and the spontaneous magnetization of powdered samples of rhombohedral Cr_2S_3 were measured. Figure 1 gives the reciprocal susceptibility as a function of temperature. The curve is characteristic for a ferrimagnet. The small value of the magnetization is the reason that the decrease of the susceptibility occurs in a

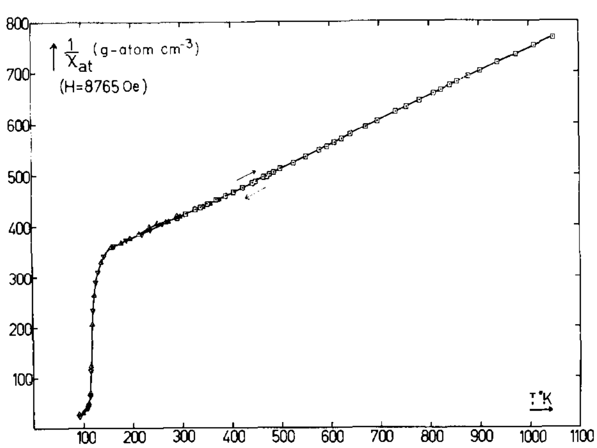

FIG. 1. Reciprocal magnetic susceptibility of rhombohedral Cr_2S_3 as a function of temperature.

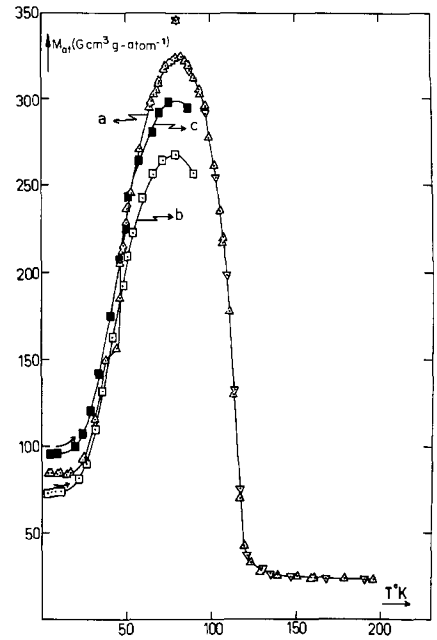

FIG. 2. Magnetization per g-atom Cr of rhombohedral Cr_2S_3.
(a) Sample not cemented (i.e., loose); $H = 8765$ Oe.
(b) Sample cemented in paraffin wax; $H = 9$ kOe.
(c) Sample cemented in paraffin wax; $H = 18$ kOe.
✡ Quenched sample.

narrow temperature region just above the Curie temperature. Between 300 and 800°K a Curie–Weiss law is satisfied, with $C_{at.} = 2.12 \pm 0.01$ cm^3 °K g-atom^{-1} (compare the spin-only value for Cr^{3+} $S = 3/2$: $C_{at.} = 1.88$ cm^3 °K g-atom^{-1}) and $\theta = -585 \pm 3$°K.

The magnetization as a function of temperature is given in Fig. 2. Below the Curie temperature $T_C = 120$°K there is a small spontaneous magnetization, with a maximum at about 85°K. The curves are all reversible between 4 and 200°K. The anomaly at 45°K, present in the loose sample (curve *a*), is absent in the cemented samples (curves *b* and *c*). The higher magnetization in the loose sample (curve *a*) is due to the orientation of the crystallites by the applied magnetic field. Quenching of the sample in silicone oil of −50°C after heating for three days at 800°C in an evacuated thin-walled silica vessel resulted in a 7% increase of the magnetization.

Figure 3 shows the magnetization as a function of magnetic field at low temperatures; the curve extrapolated to $H = 0$ gives a spontaneous magnetization of 51 G cm^3 g-atom^{-1}, which corresponds to 0.91×10^{-2} μB per Cr atom. This result does not agree with the data of Bertaut et al. (*7*), who reported a com-

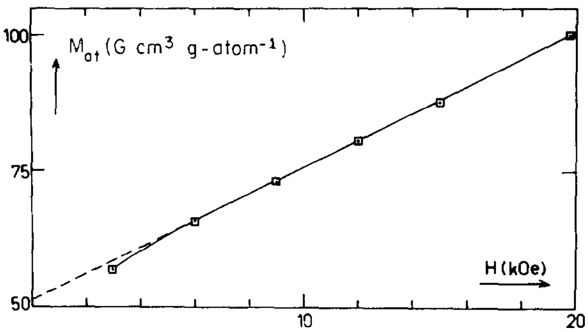

FIG. 3. Magnetization per g-atom Cr of rhombohedral Cr_2S_3 at 4.3°K (sample cemented in paraffin wax).

plete disappearance of the weak magnetism at absolute zero.

The observed magnetization can be attributed partly to a difference in the temperature dependence of the three magnetic sublattices. Such an effect would lead to zero magnetization at T_C and at T = 0°K, and explains the observed maximum in a natural way. The fact that the magnetization does not vanish at low temperature, indicates that other effects also contribute, for example an unequal occupancy of the various magnetic sublattices by Cr atoms.

Measurements by Bertaut et al. (7) show a disappearance of the magnetization at low temperature after quenching. This effect was not observed in our samples; the difference might be due to differences in composition or purity of the sample.

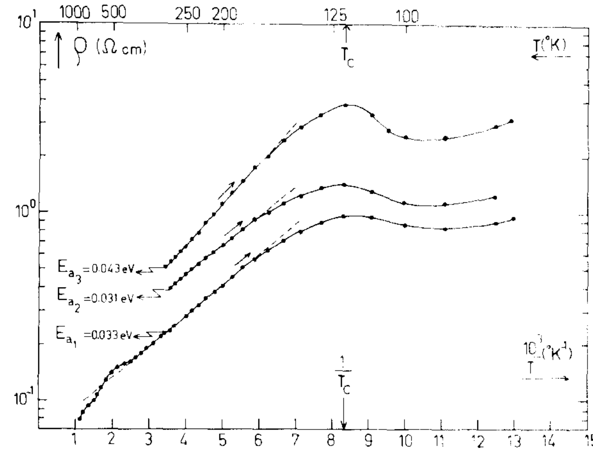

FIG. 4. Electrical resistivity ρ of three different samples 1, 2, and 3 of rhombohedral Cr_2S_3.

Electrical Properties

The results of measurements of the electrical properties of hot-pressed polycrystalline samples of *n*-type rhombohedral Cr_2S_3 are given in Figs. 4–9. Figure 4 shows the resistivity ρ as a function of temperature for three different samples. The resistivity has a maximum at the Curie temperature and a minimum at about 85°K. Between 160 and 350°K, ρ decreases exponentially with a small activation energy. The Seebeck effect (Fig. 5) shows a complicated dependence on temperature above T_C and a decrease below T_C.

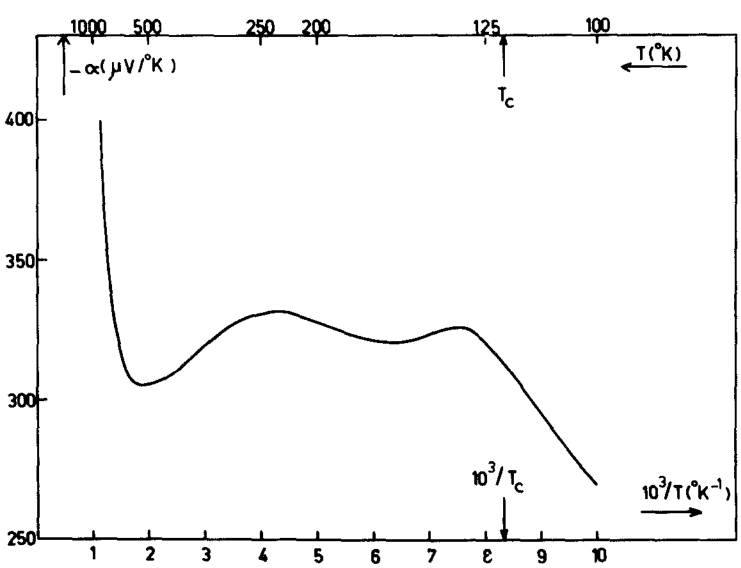

FIG. 5. Thermoelectric power α of rhombohedral Cr_2S_3 (sample 1).

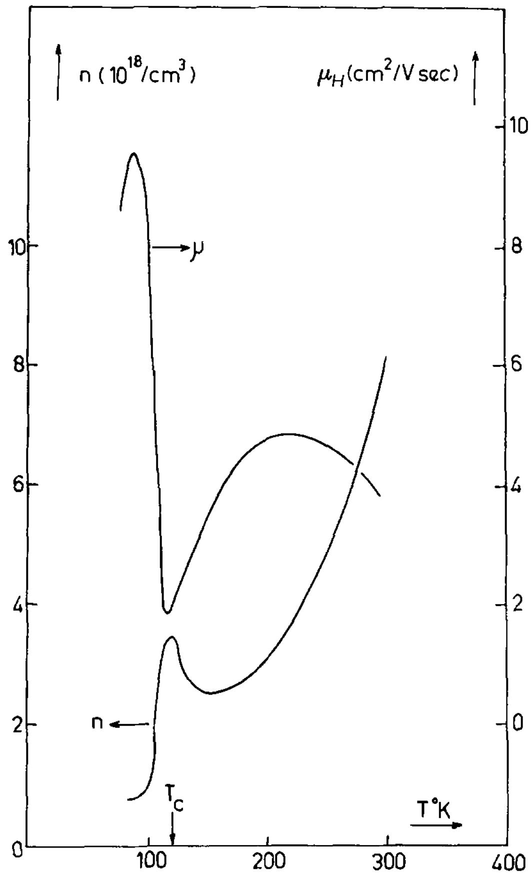

FIG. 6. Free carrier concentration n and Hall mobility μ_H, calculated from Hall and resistivity data (sample 1).

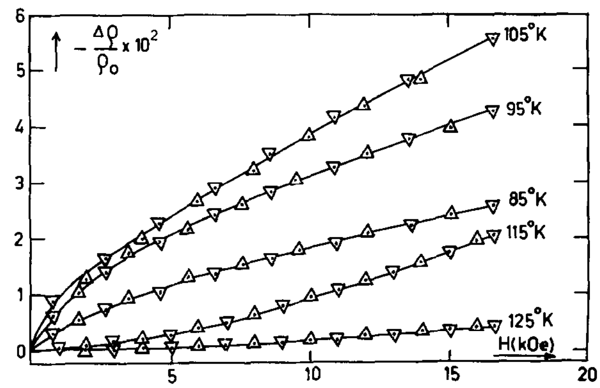

FIG. 7. Negative transverse magnetoresistance $-\Delta\rho/\rho_0$ as a function of magnetic field for T < 125°K (sample 3).

▽ indicates increasing; △ decreasing magnetic field.

Measurements showed no significant field dependence of the Hall coefficient both above and below T_C. For this reason the measured Hall coefficients are considered to represent the normal Hall effect, i.e., the contribution of the spontaneous Hall effect is small. This is not surprising because the magnetization in Cr_2S_3 is much smaller than in ferromagnetic semiconductors such as $CdCr_2Se_4$, where appreciable spontaneous Hall effects have been observed (*11*).

From the Hall coefficient R_H and the resistivity ρ, the Hall mobility $\mu_H = R_H/\rho$ and the carrier concentration $n = 1/R_H e$ were calculated (Fig. 6). The mobility shows a pronounced minimum at T_C, a steep rise below T_C and a maximum at about 85°K, the temperature where the magnetization has a maximum.

The results of measurements of the transverse magnetoresistance $\Delta\rho/\rho_0$ are shown in Figs. 7–9: $\Delta\rho$ is the change of the resistivity; ρ_0 is the resistivity without applied magnetic field. The isotherms of Figs. 7 and 8 indicate a field dependence of the form $-\Delta\rho/\rho_0 = \text{const } H^p$, with $1 < p \leqslant 2$ for $T > T_C$ and $0 < p < 1$ for $T < T_C$. Figure 9 shows that the magnetoresistance has a pronounced maximum close to T_C.

In order to eliminate a possible influence of parasitic thermomagnetic effects (*12*) on the magnetoresistance data, measurements of $\Delta\rho/\rho_0$ near T_C were carried out with different values of the electrical

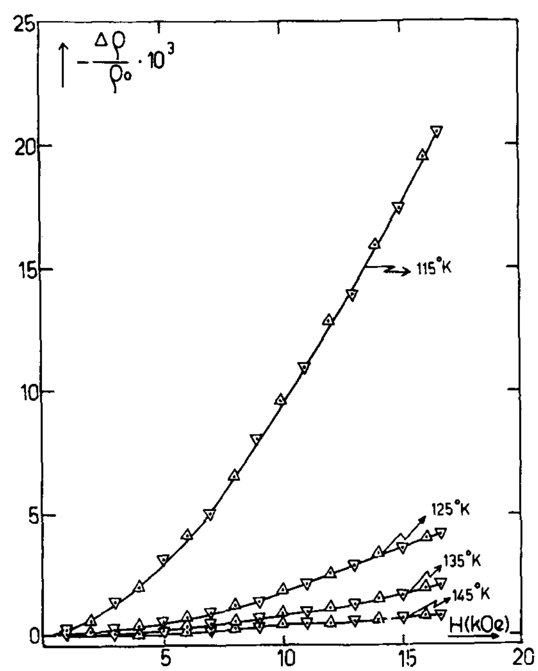

FIG. 8. Negative transverse magnetoresistance $-\Delta\rho/\rho_0$ as a function of magnetic field for T > 115°K (sample 3).

▽ indicates increasing; △ decreasing magnetic field.

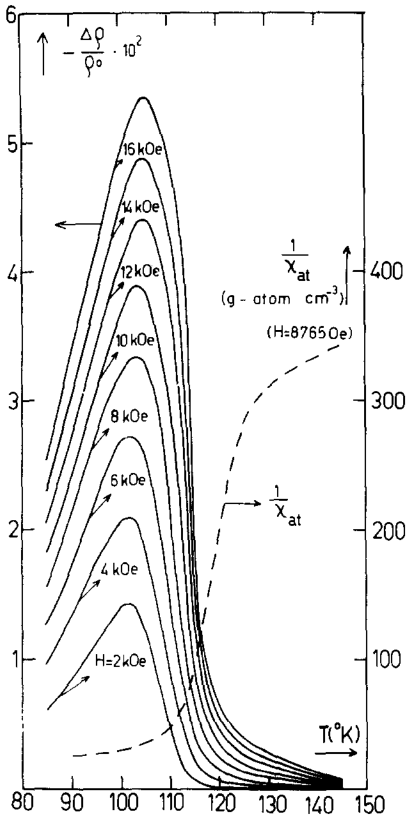

FIG. 9. Negative transverse magnetoresistance $-\Delta\rho/\rho_0$ as a function of temperature (sample 3); for comparison the $1/\chi$ versus T curve is included.

current and with increasing and decreasing magnetic field. Within the limits of experimental accuracy, no disturbing effects could be detected.

Discussion

The anomalous temperature dependence of n and μ_H (Fig. 6) and the magnetoresistance (Fig. 9) show that the magnetic properties have a large influence on the transport properties of n-type rhombohedral Cr_2S_3. Similar effects have been observed in other magnetic semiconductors, i.e., in europium chalcogenides (*13*) and in ferromagnetic chalcogenide spinels (*11, 14*).

The effects in $CdCr_2Se_4$ have been discussed in terms of an exchange interaction between the spins of the charge carriers (presumably present in a broad energy band) and the localized magnetic moments (*14, 15*). Such an interaction leads to a spin splitting of the conduction band (Fig. 10):

$$\epsilon^{\pm}(k) = \frac{\hbar^2 k^2}{2m^*} \mp \tfrac{1}{2}JS(M/M_0), \qquad (1)$$

where m^* is the effective mass and k the wave vector

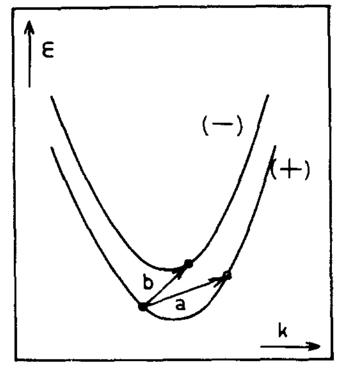

FIG. 10. Spin splitting of the conduction band, and spin-disorder scattering in a magnetic semiconductor. (a) Scattering without spin-flip; (b) scattering with spin-flip.

of the charge carriers, and S the spin of the localized magnetic moments. $\epsilon^+(k)$ represents the energy of electrons with spin parallel, $\epsilon^-(k)$ the energy of electrons with spin antiparallel to the magnetization M. M_0 is the value the magnetization would have if all localized magnetic moments were oriented parallel to one another. J is essentially an intra-atomic exchange constant; for chromium sulfides one expects J to be of the order of 0.5 eV (*14*).

The exchange interaction also leads to spin-disorder scattering of the charge carriers; a calculation of this type of scattering for magnetic semiconductors (*15*) predicts a pronounced minimum of the mobility at T_C due to the scattering at critical fluctuations. The theory also predicts a large negative magnetoresistance at the Curie temperature. Thus, the anomalous electrical properties of n-type rhombohedral Cr_2S_3, i.e., the minimum of μ_H and the maximum of the magnetoresistance at T_C, are explained at least qualitatively by the theory of spin-disorder scattering.

The fact that the spontaneous magnetization of rhombohedral Cr_2S_3 is quite small, has some important consequences for the interpretation of the transport properties. In the first place, it causes the spontaneous Hall effect to be quite small, and this enables us to obtain the temperature dependence of n and μ_H separately. It is found that the mobility has a temperature dependence which follows quite closely the predictions of the theory, i.e., a sharp minimum at T_C, a steep rise of μ_H below T_C and a much slower rise above T_C. Such a detailed comparison has not yet been possible in ferromagnetic semiconductors such as $CdCr_2Se_4$; in these compounds the large spontaneous Hall effect makes it not possible to determine μ_H and n in the neighbourhood of T_C.

Secondly, the small magnetization of Cr_2S_3 causes the spin splitting of the conduction band to be much smaller than in ferromagnetic semiconductors. At 85°K, where the magnetization reaches a maximum of $M = 0.04$ μB/Cr atom, one expects for the spin splitting $\Delta\epsilon = \epsilon^- - \epsilon^+$ a value of the order of 0.01 eV (calculated with $S = 3/2$, $J = 0.5$ eV, $M_0 =$ 3μB/Cr atom). Thus, the spin splitting in Cr_2S_3 is of the order of kT or smaller and consequently the charge carriers will be distributed over the two subbands.

One can distinguish two types of spin-disorder scattering of charge carriers: scattering within one subband ($+ \rightarrow +$ or $- \rightarrow -$), and spin-flip scattering between the subbands ($+ \rightarrow -$ or $- \rightarrow +$) (Fig. 10). In the paramagnetic region both types of scattering contribute to the resistivity. In ferromagnetic semiconductors below T_C, the spin splitting of the conduction band is usually much larger than kT, so that practically all charge carriers will be in the lower subband. In this case, the energy of the charge carriers is not sufficient for spin-flip scattering from the lower to the higher subband, and the contribution of spin-flip scattering to the resistivity will be small. In Cr_2S_3, where the spin splitting is small, this is not the case, and spin-flip scattering will give an important contribution to the resistivity also below T_C.

At 85°K the magnetization of rhombohedral Cr_2S_3 has a maximum. Thus, the spin splitting of the conduction band will be the largest at this temperature. Since a large spin splitting reduces the possibilities for spin-flip scattering, one expects a maximum of the mobility at the temperature where the magnetization has a maximum. Such a maximum was, indeed, observed in rhombohedral Cr_2S_3 at 85°K (Fig. 6).

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References

1. F. Jellinek, *Acta Crystallogr.* **10**, 620 (1957).
2. T. J. A. Popma and C. F. van Bruggen, *J. Inorg. Nucl. Chem.* **31**, 73 (1969).
3. A. W. Sleight and T. A. Bither, *Inorg. Chem.* **8**, 566 (1969).
4. C. F. van Bruggen, Thesis, Groningen, 1969.
5. C. F. van Bruggen and F. Jellinek, "Prop. Thermodyn. Phys. et Struct. des Dérivés Sémi-métalliques," CNRS, p. 31, Paris, 1967.
6. C. F. van Bruggen, *Third Int. Conf. Solid Compounds of Transition Elements, Oslo* 36 (1969).
7. E. F. Bertaut, J. Cohen, B. Lambert-Andron, and P. Mollard, *J. Phys. Paris* **29**, 813 (1968).
8. T. J. A. Popma and C. Haas, *Third Int. Conf. Solid Compounds of Transition Elements, Oslo* 39 (1969).
9. T. J. A. Popma, B. van Laar, and C. Haas, *J. Phys. Chem. Solids*, to be published.
10. T. J. A. Popma, Thesis, Groningen, 1970.
11. H. W. Lehmann, *Phys. Rev.* **163**, 488 (1967).
12. R. A. Smith, "Semiconductors," Chap. 6, Cambridge University Press, 1959.
13. S. Methfessel and D. C. Mattis, Magnetic semiconductors, *in* "Encyclopedia of Physics," Vol. XVIII/1, pp. 389–562 (H. P. J. Wijn, Ed.), Springer Verlag, Berlin, 1968.
14. C. Haas, A. M. J. G. van Run, P. F. Bongers, and W. Albers, *Solid State Commun*, **5**, 657 (1967).
15. C. Haas, *Phys. Rev.* **168**, 531 (1968).