

The Magnetic and Electrical Properties of LnCrSe_3 ($\text{Ln}=\text{La, Ce, Pr, Nd}$)

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Magnetic and electrical measurements have been made on single crystals and polycrystalline samples of LnCrSe_3 , where Ln is lanthanum, cerium, praseodymium and neodymium. These materials are all anti-ferromagnetic, but show weak ferromagnetism at lower temperatures. The resistivity and Hall effect show these compounds to be extrinsic semiconductors.

Introduction

A number of ternary compounds of transition metal rare earth chalcogenides have been prepared and studied. Among these are several groups of compounds which have analogous structures such as the spinel type MLnX_4 , the orthorhombic MLn_2X_4 with the MnY_2S_4 structure, and the MLn_4S_7 phases of the FeY_4S_7 structure type (1). These phases, which have divalent transition metals, have properties that are similar to the rare earth sesquisulfides, such as paramagnetic behavior due to localized electrons (2). In contrast, those compounds which have the transition metal in a trivalent state (3-5) would be expected to exhibit completely different physical properties. One series of compounds within this group is LnCrSe_3 , where Ln is lanthanum, cerium, praseodymium and neodymium. The magnetic properties of these compounds are similar to those exhibited by the ternary oxides of the type LnCrO_3 . Of greater interest and importance is the relationship between the observed magnetic properties and the crystal structure.

Experimental

Preparation of Materials

In order to prepare the LnCrSe_3 powders, equimolar amounts of Cr_2Se_3 and Ln_2Se_3

were reacted (3, 4). Whereas Cr_2Se_3 was always prepared by heating stoichiometric proportions of the elements, two methods were used to prepare the Ln_2Se_3 . The first method was to react the corresponding rare earth oxide with H_2Se at 1200°C , and the second was by direct combination of the elements in an evacuated silica tube. The two selenides were then mixed thoroughly, pressed into pellets, and fired at 1000°C for varying amounts of time (between 4 days and 2 mo).

The single crystals of these materials used in this study were prepared from a melt of LnI_3 (3, 5). The reactants and flux were combined in the ratio $4 \text{ LnI}_3/1 \text{ Ln}_2\text{Se}_3/0.70 \text{ Cr}_2\text{Se}_3$. Cr_2Se_3 was first prepared by direct combination of the elements and then added to a special reaction chamber (3), whereas the LnI_3 and Ln_2Se_3 were formed directly in the chamber by reaction of the elements. After the reaction tube was sealed, it was heated to about 800°C in order to form the single crystals of the LnCrSe_3 .

Characterization of the Materials

X-Ray Data. Crystallographic data for the four compounds of the type LnCrSe_3 are given in Table I. A complete structural analysis was performed on CeCrSe_3 using Weissenberg and precession techniques with $\text{Mo}(K\alpha)$ radiation. The compound was found to be orthorhombic

TABLE I

	a (Å)	b (Å)	c (Å)	d_{calcd} (g/cm ³)	d_{obsd} (g/cm ³)
LaCrSe ₃	8.11 ± 0.01	13.79 ± 0.02	3.96 ± 0.01	6.41	6.35
CeCrSe ₃	8.080 ± 0.005	13.741 ± 0.010	3.952 ± 0.003	6.52	6.47
PrCrSe ₃	8.05 ± 0.01	13.70 ± 0.02	3.93 ± 0.01	6.58	
NdCrSe ₃	8.01 ± 0.01	13.61 ± 0.02	3.91 ± 0.01	6.70	

with the centrosymmetric space group $Pnam$ (3). Similar X-ray diffraction patterns, using $\text{Cu}(K\alpha)$ radiation were found for all four compounds listed in Table I. The slight shifts in the line positions are due to the variation in the size of the rare earth ion. The cell parameters given in Table I are from Refs. (3 and 5).

Electron Microscopy. A Cameca MEB 107 electron microscope was used to investigate the presence of impurities as well as determine the homogeneity within a sample. In addition it was possible to compare the relative amounts of chromium in three samples of CeCrSe₃, PrCrSe₃, and LaCrSe₃.

Samples were examined for impurity peaks of iodine and silver which might be the most likely contaminants. Maximum sensitivity failed to reveal the presence of either of these elements. A scanning technique was used to verify that the surface of the sample was homogeneous with respect to chromium content. The relative intensities of the $\text{Cr}(K\alpha_1)$ peaks were observed in order to compare the relative amounts of chromium in these compounds, and the values obtained were

	Counts/sec of $\text{Cr}(K\alpha_1)$ peak
CeCrSe ₃	2300 ± 100
PrCrSe ₃	2600 ± 100
LaCrSe ₃	2500 ± 100

The slightly low value for CeCrSe₃ was probably due to small pits which were observed in the crystal, rather than a deficiency of Cr in the compound.

Magnetic Measurements

Magnetic measurements were made with a Faraday balance which has been described by Barthélemy (2). For the measurements between 77 and 800 K both polycrystalline samples and

single crystals were used, and measurements were made down to 10 K on single crystals of LaCrSe₃ and PrCrSe₃.

Measurements on the single crystals were also attempted at 4.2 K with a Foner magnetometer; however, the value of the magnetic moment ($<10^{-3} \mu_B$) was too small to detect with the instrument.

Electrical Measurements

Measurements of the resistivity and Hall voltage were made between 77 and 400 K. The resistivity was measured by a direct current four-probe method, and the Hall voltage was measured by an alternating current method which has been described in the thesis of Lee (8). The single crystals were in the form of prisms with the c -axis having the longest dimension. Therefore the current for both the resistivity and Hall measurements was parallel to the c -direction. Attempts were made to measure the resistivity along other crystallographic directions, but due to the morphology of the crystals (needles, $\sim 4 \times 1 \times 1$ mm) it was not possible to observe the anisotropy which might be expected for this structure.

Electrical contacts were made to the samples by attaching ultrasonically bonded indium leads to the samples. The samples were then mounted on an alumina substrate by soldering the indium leads to silver solder terminals on the alumina pads. Teflon coated copper wires were connected to the pads to make the electrical connection to the external equipment. The alumina pads were cemented to a copper block to insure thermal equilibrium during the measurements.

Results and Discussion

The results of the magnetic measurements are given in Figs. 1 and 2 and summarized in Table II. In some cases, different temperatures were obtained for the appearance of the weak ferro-

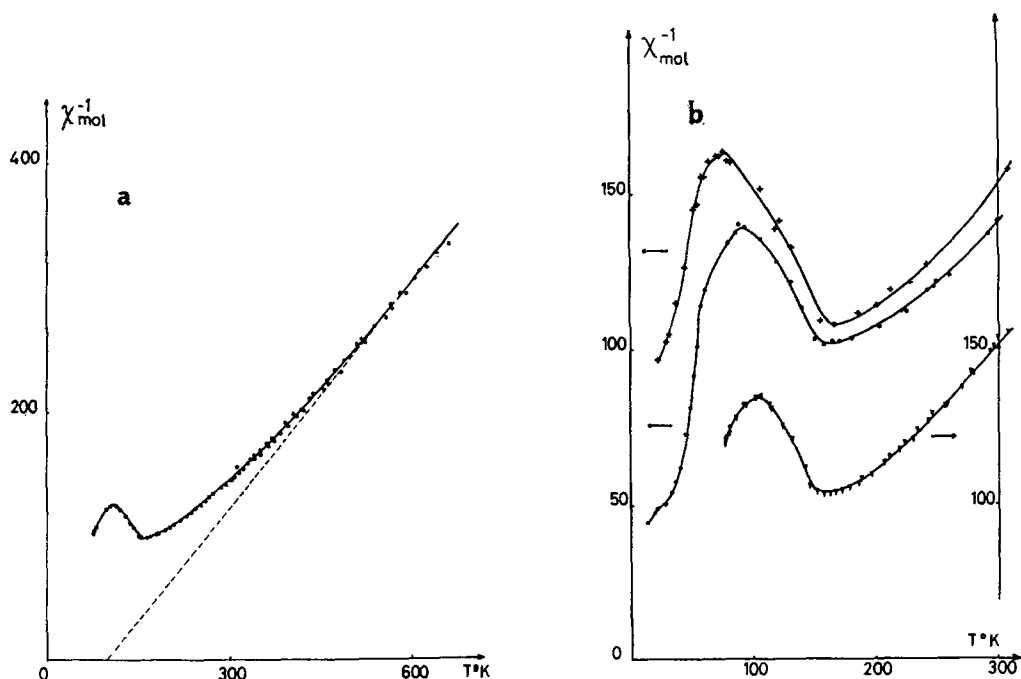


FIG. 1. The reciprocal molar susceptibility in emu versus absolute temperature for LaCrSe_3 . (a) Powder; (b) (+ and ●) single crystals, (▼) powder.

magnetic behavior (T_f , the maximum of $1/x$ vs T) for different samples of the same compound, probably as a result of small undetectable changes in stoichiometry or purity; however, the Néel point was always observed at the same temperature for different samples of the same

compound. The observed differences in T_f could not be correlated with the different methods of preparation described in the previous section.

The results of the susceptibility measurements on LaCrSe_3 are shown in Fig. 1 and Table II. These results have been corrected for core

TABLE II^a

	Method of preparation ^b	θ_p (K)	T_n (K)	T_f (K)	μ_{eff}	μ_{calc}
LaCrSe_3	A ₁	+99	160	110	3.61	3.87
	A ₄	—	160	107		
	A ₂ , A ₃ , B ₁ , B ₂ , C ₃	—	160	<77		
	C ₂	—	165	90		
	C ₁	—	167	77		
CeCrSe_3	A ₁	+50	171	130	4.29	4.64
	B ₁	—	175	135		
PrCrSe_3	A ₁ , C ₁	+10	(170)	(160–165)	5.11	5.30
NdCrSe_3	A ₁	-25	(183)	(160)	5.22	5.34

^a θ_p , paramagnetic Curie temperature; T_n , Néel temperature; T_f , Maximum in $1/x$ vs T curve; μ_{eff} , measured effective moments per mole (in Bohr magnetons); μ_{calc} , calculated magnetic moment (spin-only by formula $\mu = gJ[J(J+1) + J'(J'+1)]^{1/2}$ where Landé factor $g = 2$); J , quantum number for rare earth; J' , quantum number for Cr^{3+} .

^b Method of preparation: A_x, rare earth selenide prepared by action of H_2Se on rare earth oxide; B_x, rare earth selenide prepared by reaction of elements in an evacuated silica tube; C_x, single crystal prepared by method described in Ref. (1).

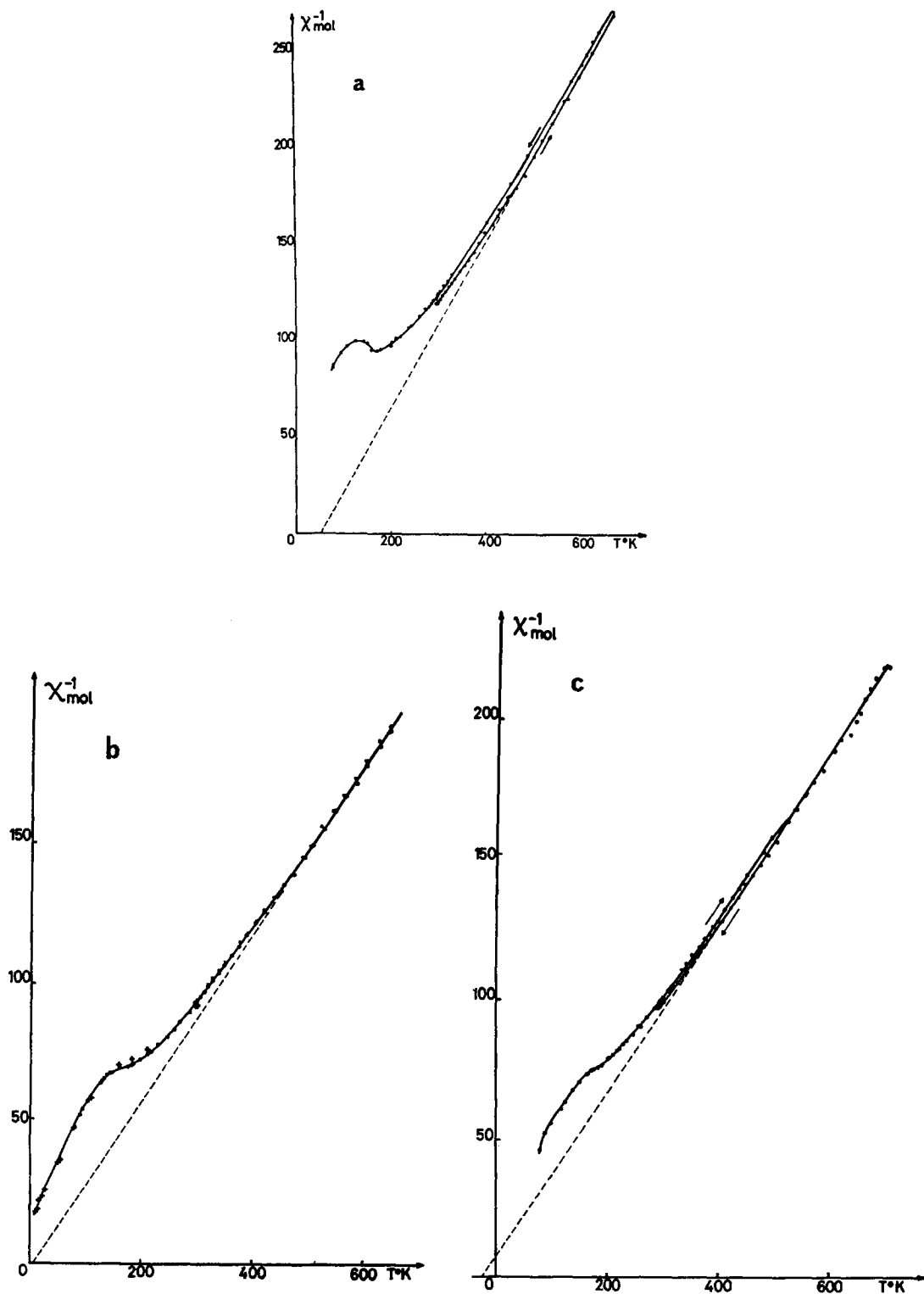


FIG. 2. The reciprocal molar susceptibility in emu versus absolute temperature for (a) CeCrSe₃, (b) PrCrSe₃, (c) NdCrSe₃.

diamagnetism. The Curie constant found for Cr^{3+} in this compound is only slightly smaller than that calculated for the free Cr^{3+} ion from the spin-only moment $(g[J(J+1)]^{1/2})$, where $J=S$ as would be expected since La^{3+} is diamagnetic. The Néel temperature is almost constant for all samples, and is near 160 K. However, at lower temperatures, between 60 and 110 K, a very weak ferromagnetism is observed. This type of behavior may be similar to that observed in other rare earth chromites (9).

The curves for the Ce, Pr and Nd compounds are shown in Fig. 2. In the paramagnetic region above the Néel temperature there is a contribution to the paramagnetic behavior from both the Cr^{3+} and the rare earth ion. Below the Néel temperature, the observed magnetic susceptibility has an antiferromagnetic contribution from the Cr^{3+} , and a paramagnetic contribution from the rare earth. Therefore, by subtracting the contri-

bution from the rare earth ion from the total moment, the magnetic behavior of Cr^{3+} in the Ce, Pr, and Nd analogues is found to be similar to that found for Cr^{3+} in the compound LaCrSe_3 . In Table II, the observed values of the effective magnetic moments are compared with the values calculated from the spin-only contribution of Cr^{3+} and the spin and orbital contributions of the trivalent rare earth ions. In addition, it should be noted that the Weiss constant is positive for the La, Ce, and Pr compounds (see Table II), indicating the possible presence of ferromagnetic interactions at temperatures above the Néel point.

In these materials the chromium ion is at the center of an octahedron with a slightly distorted base. The Cr-Se distances vary between 2.50 and 2.59 Å. The CrSe_6 units are edge-sharing, and form continuous chains in the z -direction, as shown in Fig. 3. These chains are separated

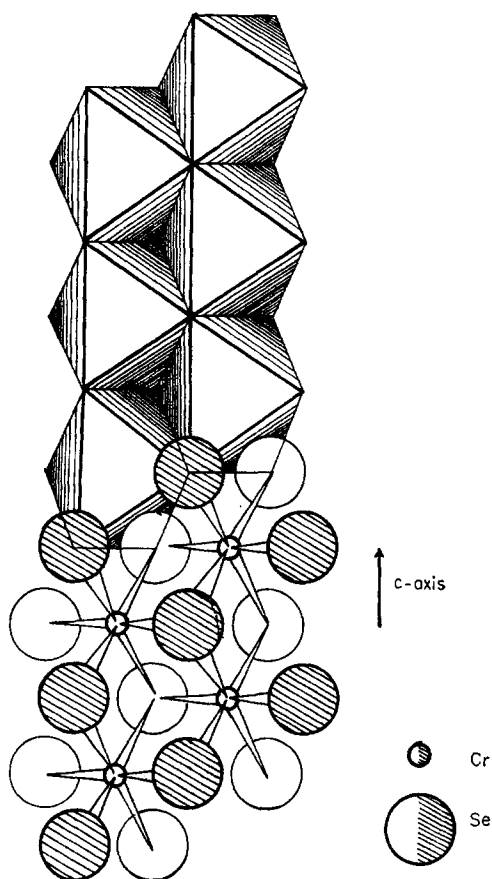


FIG. 3. The structure of the CrSe_6 units in CeCrSe_3 along the c -axis. The small circles represent chromium and largest are the selenium atoms.

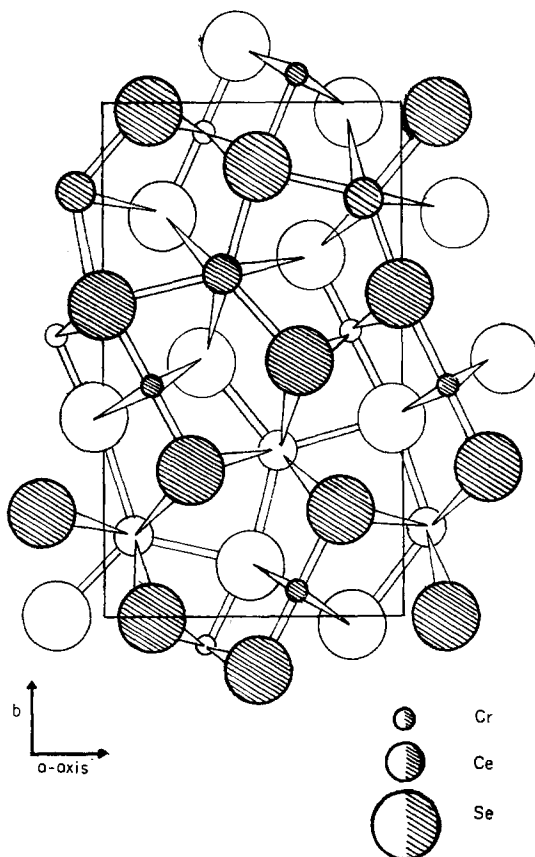


FIG. 4. The structure of CeCrSe_3 . The dark atoms are at $z = 3/4$, the lighter atoms are at $z = 1/4$. The smallest circles represent chromium, the intermediate are the lanthanide atoms and the largest are the selenium atoms.

from each other by LnSe₃ polyhedra. It can also be seen from Fig. 4 that two chromium ions are located on the opposite corners of a parallelogram 2.50 and 2.55 Å on an edge, with selenium ions on the other two corners as shown in Fig. 4. The angle of interaction for indirect exchange through the selenium ions is found to be 88°25', with a direct Cr–Cr distance of 3.52 Å, which is larger than the 3.48 Å calculated by Goodenough (10) as the critical distance for delocalization of the orbitals. The next-nearest Cr–Cr distance, in the z-direction, is also short, 3.95 Å. This zigzag chain of Cr ions is separated from the next-nearest chain by 7.97 Å, center to center, and the second-nearest chain by 8.08 Å.

There are then two types of magnetic interactions which are possible in this structure (11): antiferromagnetic Cr–Cr interactions which decrease sensitively with increasing Cr–Cr separation and ferromagnetic 90° Cr–Se–Cr interactions which increase with the Cr-anion covalent mixing. The Cr–Se–Cr interactions should dominate the Cr–Cr interaction, as in CdCr₂Se₄, making the net coupling between the localized

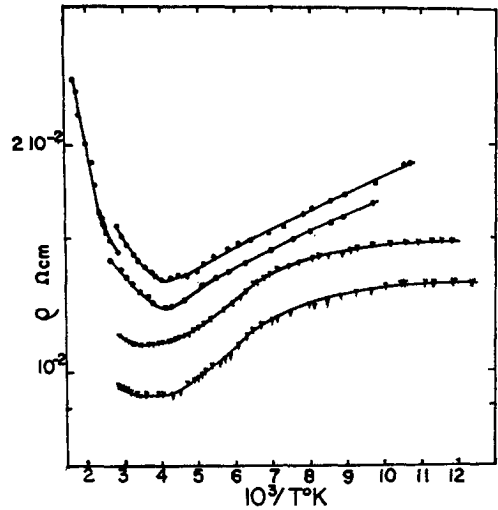


FIG. 6. The resistivity versus 10^3 over the absolute temperature for LaCrSe₃ (▼) and PrCrSe₃ (●) single crystals.

Cr³⁺ ion spins within the z-axis chains ferromagnetic. Between the chains there is a possibility of antiferromagnetic Cr–Se–Se–Cr interactions (12) so that the chains are aligned antiparallel with respect to each other. Such a Cr–Se–Se–Cr interaction in ZnCr₂Se₄ creates an antiferromagnetic spiral, even though ferromagnetic nearest-neighbor interactions give a positive Weiss constant, as in LnCrSe₃.

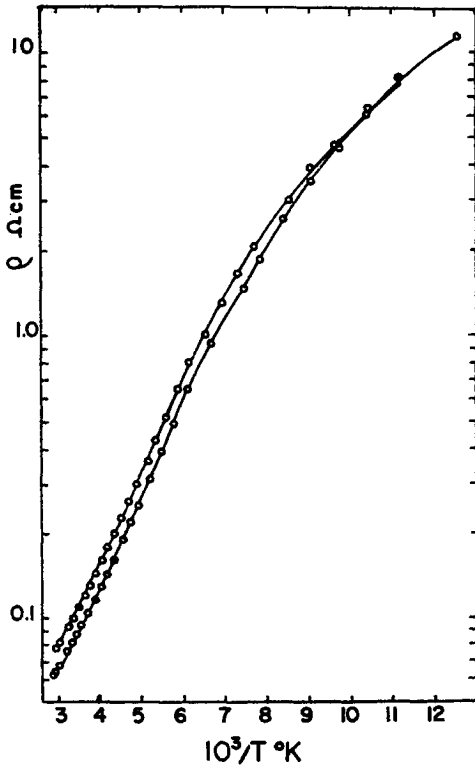


FIG. 5. The resistivity versus 10^3 over the absolute temperature for CeCrSe₃ single crystals.

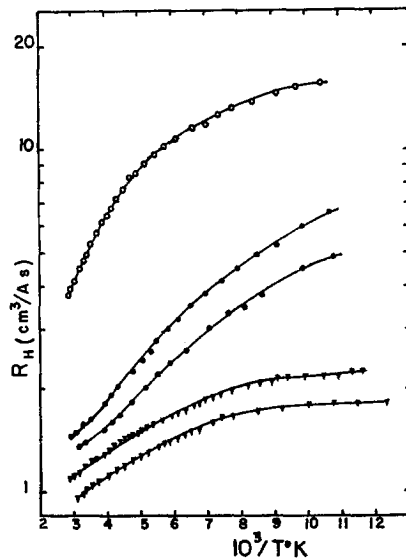


FIG. 7. The Hall coefficient versus 10^3 over the absolute temperature for CeCrSe₃ (○), LaCrSe₃ (▼), and PrCrSe₃ (●) single crystals.

TABLE III

	LaCrSe ₃		CeCrSe ₃		PrCrSe ₃		NdCrSe ₃	
	77 K	300 K	77 K	300 K	77 K	300 K	77 K	300 K
$\rho(\Omega \text{ cm})$	1×10^{-2}	1.4×10^{-2}	10	1×10^{-2}	2×10^{-2}	1.5×10^{-2}	5×10^{-2}	6×10^{-2}
$\frac{1}{R_H \times e}$	2×10^{18}	6×10^{18}	2×10^{17}	1×10^{18}	1×10^{18}	5×10^{18}	—	—
$\mu_H(\text{cm}^2/\text{v sec})$	150	100	3	70	400	100	—	—

Therefore, at temperatures above the Néel point, the positive Weiss constant indicates ferromagnetic intrachain interactions, and deviation from a Curie-Weiss law well above T_N indicates the probable presence of extensive short-range ferromagnetic Cr–Se–Cr interactions within the chains. As the temperature is lowered through T_N , the longer-range antiferromagnetic

interactions between the chains become dominant. At still lower temperatures, there may be a canting of the spins which would give rise to a weak ferromagnetism. Although this model is consistent with the experimental results, neutron diffraction data are necessary before the exact nature of the magnetic interactions can be ascertained.

The results of the resistivity measurements on these compounds are given in Figs. 5 and 6 in Table III. The measurements on LaCrSe₃, CeCrSe₃, and PrCrSe₃ were made on single crystals. The variation of the resistivity with temperature is very small in the La and Pr compounds and shallow minimums are observed in these curves. In CeCrSe₃, the resistivity increases with decreasing temperature. There are no observable effects on the resistivity at the temperatures where the magnetic transitions occur.

The Hall coefficients (R_H) of the La, Ce, and Pr compounds are shown in Fig. 7 and Table III. The value of $1/R_H e$ is of the order of 10^{17} to 10^{19} cm^{-3} , and all samples had a positive value for R_H . The temperature dependence of the Hall mobilities calculated from the Hall and resistivity data is shown in Fig. 8. Thus these materials are all extrinsic semiconductors in the temperature region of the electrical measurements, even up to 300°C in the case of the La and Pr compounds.

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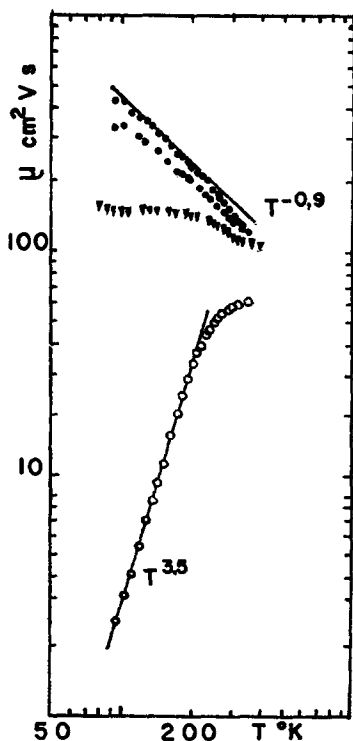


FIG. 8. The Hall mobility versus absolute temperature for CeCrSe₃ (○), LaCrSe₃ (▼), and PrCrSe₃ (●) single crystals.

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