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# Investigation of the ferromagnetism in $RCrSb_3$ (R=La, Ce, Pr, Nd)

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## Abstract

Magnetization and electrical resistivity measurements of the polycrystalline $RCrSb_3$, R=La, Ce, Pr, and Nd, were carried out using SQUID magnetometry and the four probe method in the temperature range of 2 to 400 K and at fields of up to 5.5 T. All compounds are found to exhibit ferromagnetism at temperatures above 100 K as a result of the d–d interaction of the chromium atoms. Inverse susceptibility of the mentioned compounds follows a non linear Curie–Weiss law which indicates that there is no fixed effective magnetic moment per chromium atom. Electrical resistivity of $LaCrSb_3$ was found to follow a $T^2$ law at temperatures below 38 K. The magnetoresistance of $LaCrSb_3$ is found to be 5.5% at 150 K. The ferromagnetic to paramagnetic phase transition is found to be of the second order from a capacitance dilatometer measurements.

*Keywords:* Magnetism; Antimonides; Resistivity; Magnetoresistance; $RCrSb_3$

## 1. Introduction

Among the large number of intermetallic compounds, those formed by rare earth metals and the 3d transition metals are of a considerable interest. Their magnetism is caused by the localized electrons belonging to the 4f orbital of the rare earth and the itinerant electrons in the 3d orbitals of the transition metals. As a result, the magnetic behavior of these compounds is determined by three exchange interactions, namely f–f, f–d and d–d interactions. In general, the transition metal in a 4f–3d intermetallic compound is responsible for the relatively high magnetic ordering temperatures. The existing theory allows us to describe, in most cases qualitatively, the magnetism of the well localized 4f-shells in crystals if the energy schemes of the $R^{3+}$ ions are known. Numerous experimental studies have been done to determine the crystal field parameters and the molecular field coefficients on rare earth sites [1]. However, the treatment of the magnetic phenomena of 3d-ions is more complicated since the electronic characteristics of the 3d-ions changes in metallic materials because of the itineracy of the d-electrons. Further, electronic structure of hybridized 3d electrons can differ from that of the 3d–5d electron system in intermetallic compounds. Most transition metals form binary compounds with rare earths except chromium. But a few ternary compounds of chromium and rare earths exist where the chromium atoms couple antiferromagnetically.

$RCrSb_3$ (R=La–Dy) is a newly discovered series intermetallic compounds, one of a few in which chromium orders ferromagnetically. These system has been found to crystallize in the orthorhombic structure and belongs to the space group *Pbcm* [2]. Previous results of magnetic and electronic measurements established the first member of this series as an itinerant electron ferromagnet [3]. In this paper we present magnetic properties and electrical resistivity studies on the $RCrSb_3$ with R=La, Ce, Pr and Nd. Also we have studied the first magnetoresistance of the above system. Such studies would help in better characterizing these intermetallics.

## 2. Experimental details

The proper amount of the constituent elements were arc melted under flowing Ar and repeated melted to ensure homogeneity. An excess amount of Sb (10%) was added to compensate for losses during melting. The purity of the starting elements are 99.9% rare earth elements, 99.99% Cr and 99.999% Sb. The resulting compounds were annealed at 600°C for 2 days and 800°C for 8 days and are stable in air. X-ray measurement show the polycrystalline $RCrSb_3$ contains about 12% of the phase of RSb. Magnetization measurements were performed using a SQUID magneto-

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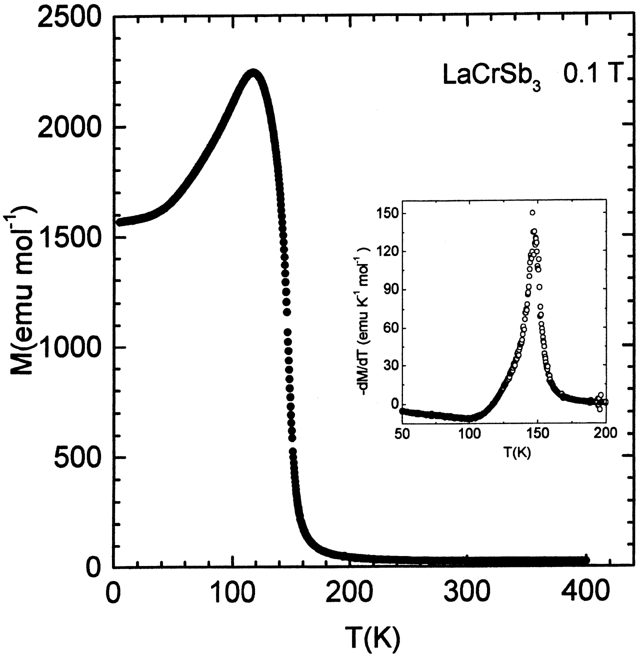


Fig. 1. Temperature ($T$) dependence of magnetization ($M$) of $LaCrSb_3$ at 0.1 T. Inset to Fig. 1 shows the negative first derivative of the magnetization ($-dM/dT$) with respect to the temperature ($T$) of $LaCrSb_3$ at 0.1 T, the peak occurs at the transition temperature.

meter in the temperature range of 5–400 K and at fields of up to 5.5 T. All samples were zero field cooled. The conventional four probe method was employed in the resistivity and magneto-resistivity measurements (in the SQUID) over the above mention ranges. The order of the phase transition was determine by capacitance dilatometry.

## 3. Results

### 3.1. Magnetization

Magnetization as a function of both temperature and field were determined for all polycrystalline samples $RCrSb_3$. Plotted in Fig. 1 is the temperature dependence of the magnetization for $LaCrSb_3$ at 0.1 T. As the sample is heated from 5 K, a transition from ferromagnetic (FM) to paramagnetic (PM) phase is observed at 146 K. This transition temperature can clearly be observed from the first derivative of the $M$ vs. $T$ curve (see inset to Fig. 1). In Fig. 2, we present a similar magnetization data for $RCrSb_3$ for magnetic R at 0.1 T. A transition from PM to FM phase can be seen above 130 K. The magnetization of $CeCrSb_3$ forms a broad peak at about 10 K, it increases with temperature for $T<T_C$. For $PrCrSb_3$ and $NdCrSb_3$, f–d exchange interaction causes an increase in the magnetization as the temperature is decreased below $T_C$. Below 50 K, competition between f–f and f–d interaction causes a sharp increase in the magnetization and then a decreases below a critical temperature. The $T_C$ for these compounds were also obtained from the first derivative of the $M$ vs. $T$ curve, and are shown in Table 1. These temperatures are slightly larger than the values reported by Hartjes et al. [4] by about 20–30 K. This difference can be caused by the decrease in lattice constants by about 0.5% (Table 1) compared to values in reference [2]. Since the size of the unit cell is smaller, the nearest neighbor distance is decrease thereby increasing the exchange interaction. We attribute $T_p$ the lower critical temperature to RSb phase which is present in our sample. The inverse susceptibiliy was fitted by a modified Curie–Weiss law of the form

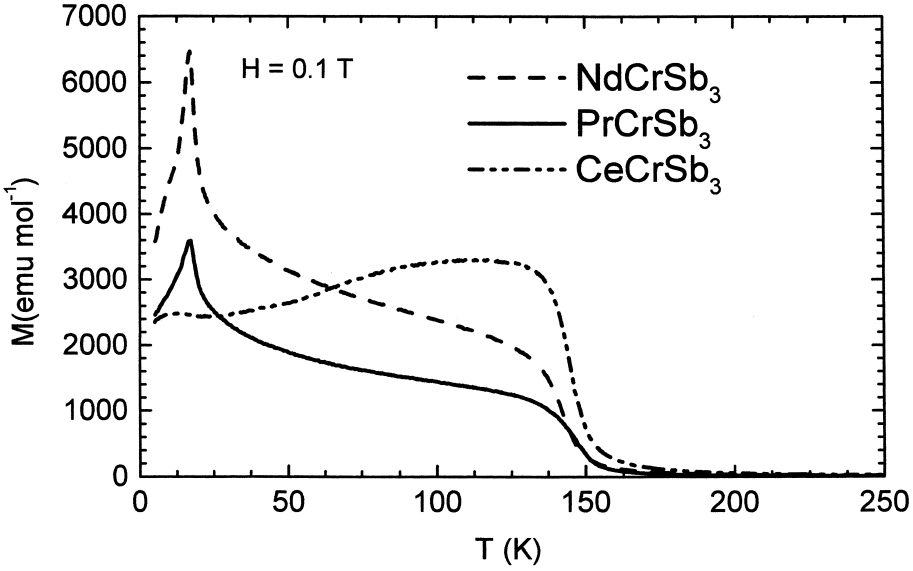


Fig. 2. Magnetization ($M$) of $CeCrSb_3$, $PrCrSb_3$, and $NdCrSb_3$ as a function of temperature ($T$) at 0.1 T. The actual magnetization of $CeCrSb_3$ is increased by a factor of 1.5 and that of $PrCrSb_3$ is reduced by the same factor to fit into the same plot.

Table 1
Some basic magnetic characteristics and cell parameters of $RCrSb_3$ compounds

| Compound | $p_{eff}$ ($\mu_B$) | $\mu_{5.5T}$ ($\mu_B$) | $T_C$ (K) | $T_p$ (K) | $a$ (Å) | $b$ (Å) | $c$ (Å) |
|---|---|---|---|---|---|---|---|
| $LaCrSb_3$ | 2.60 | 1.11 | 146 | – | 13.188 (4) | 6.159 (1) | 6.069 (1) |
| $CeCrSb_3$ | 3.38 | 2.08 | 145 | 10 | 13.078 (1) | 6.1744 (6) | 6.0725 (5) |
| $PrCrSb_3$ | 3.83 | 2.19 | 147 | 17 | 12.959 (1) | 6.1509 (5) | 6.0497 (4) |
| $NdCrSb_3$ | 4.15 | 2.35 | 142 | 17 | 12.979 (1) | 6.1847 (5) | 6.0664 (5) |

$\chi=\chi_o+C/(T-\theta)$ in the temperature range 200–400 K. The values of the magneton numbers ($p_{eff}$) obtained from the Curie constant are shown in Table 1, these values are not in agreement with calculated values for the free ions, which imply that there is no fixed effective magnetic moment per chromium atom.

The magnetization of $RCrSb_3$ were determined as a function of an externally applied field at constant temperatures. The isotherms of magnetization characterize regions of paramagnetic and magnetically ordered states of $RCrSb_3$ and are shown in Figs. 3 and 4. We have tabulated the magnetization obtained at the highest field of 5.5 T in Table 1.

### 3.2. Resistivity

Electrical resistance of all compounds were measure at zero field as a function of temperature. The resistivity follows a $T^2$ law at low temperatures for $LaCrSb_3$ (Fig. 5b) and deviates before the Curie temperature is reached. The temperature dependence of the reduced resistivity is altered at the ferromagnetic critical points for all the compounds as can be seen in Fig. 5a, moreover, the inset shows another change in the resistivity at temperatures below 24 K corresponding to the low temperature magnetic phase transition seen in compounds with R=Pr and Nd. These critical points are in the neighborhood of both the critical temperature, and so confirms the magnetic transitions. The resistivity of $LaCrSb_3$ as a function of an external field is shown as an inset in Fig. 5b, the value of magnetoresistance, $(\rho(H)-\rho(0))/\rho(0)$, obtained is 5.5% at 150 K.

### 3.3. Relative thermal expansion

In order to determine the order of the phase transition, the relative change in the length of the polycrystalline samples were measured as a function of the temperature (Fig. 6). The sole purpose of this measurement is to determine the order of the FM to PM phase transition, and it is found to be of the second order.

## 4. Discussion

Ferromagnetic magnetic ordering temperature in $RCrSb_3$ compounds is caused by the d–d exchange interaction between the chromium atoms. Below the transition temperature the predominant interaction mechanism is the f–d interaction as the effective field of the chromium causes

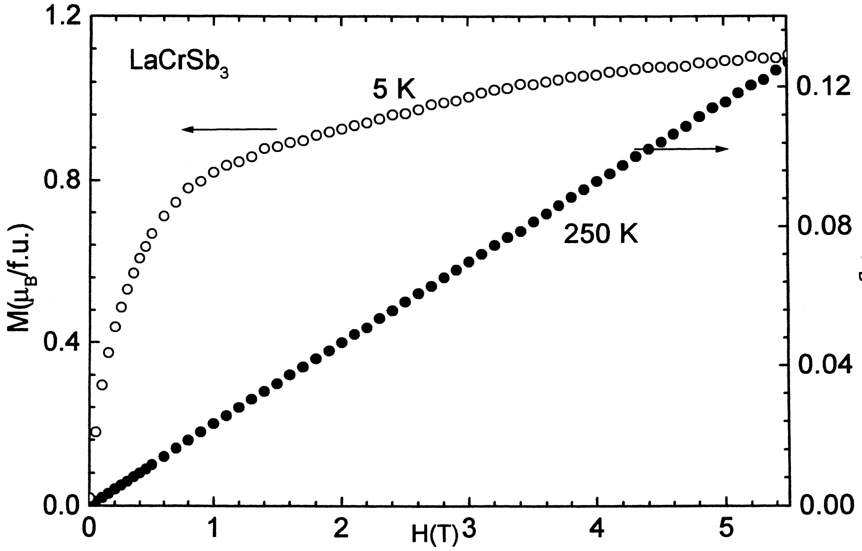


Fig. 3. Magnetization ($M$) as a function of applied magnetic field ($H$) at 5 and 250 K of $LaCrSb_3$ showing regions of ferromagnetic and paramagnetic phases.

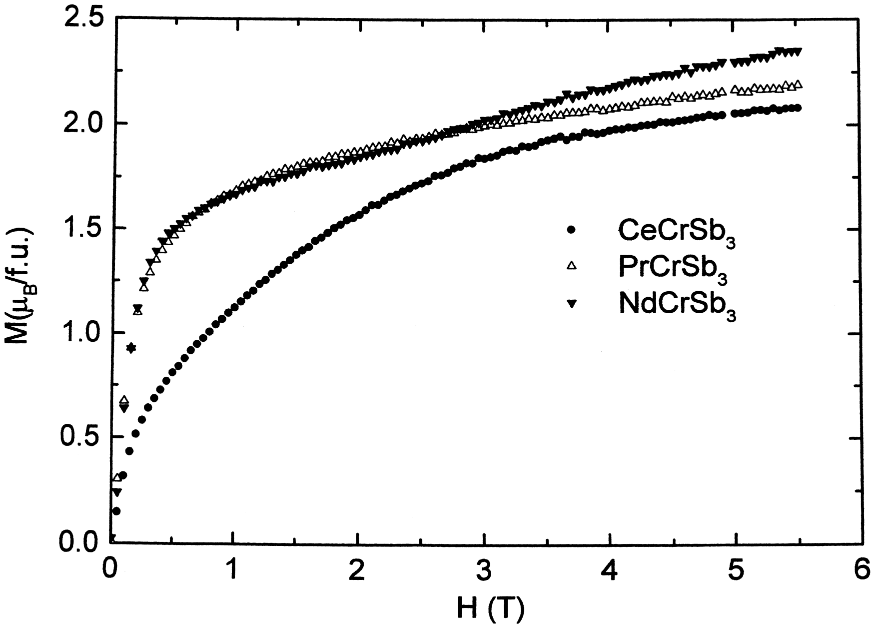
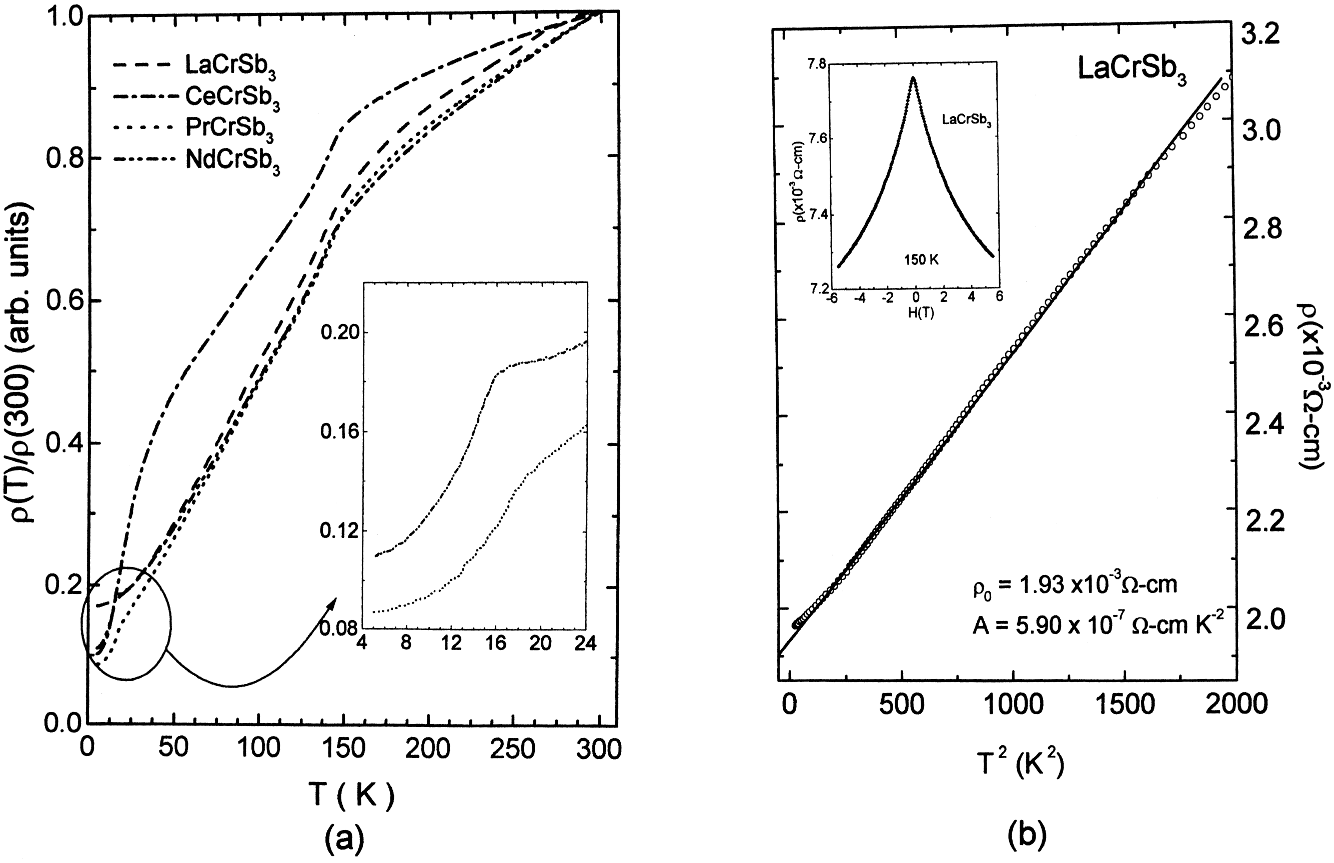


Fig. 4. Magnetization ($M$) as a function of applied magnetic field ($H$) $CeCrSb_3$, $PrCrSb_3$, and $NdCrSb_3$ at 5 K. Observe the change in the magnetization of $NdCrSb_3$ near 2.5 T.



(a)

(b)

Fig. 5. (a) Relative resistivity ($\rho(T)/\rho(300\text{ K})$) of $LaCrSb_3$, $CeCrSb_3$, $PrCrSb_3$, and $NdCrSb_3$ as a function of temperature ($T$). The low temperature region is enlarge in the inset to show a change in the resistivity at temperatures corresponding to the magnetic transition temperatures. (b) Shows the a linear dependency of the resistivity ($\rho$) of $LaCrSb_3$ on the square of the temperature ($T^2$). The inset shows the variation of the resistivity ($\rho$) of $LaCrSb_3$ as a function of applied magnetic field ($H$) at 150 K.

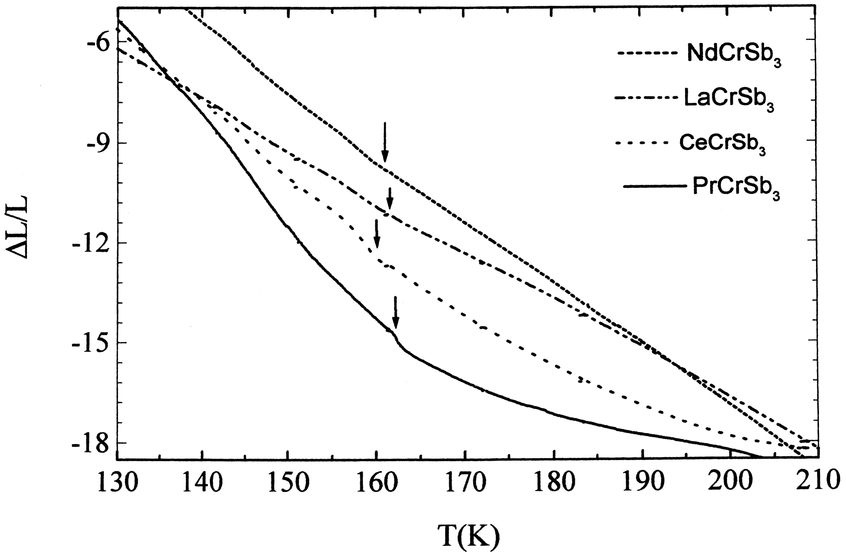


Fig. 6. Relative thermal expansion ($\Delta L/L$) of $LaCrSb_3$, $CeCrSb_3$, $PrCrSb_3$, and $NdCrSb_3$ as a function of temperature ($T$).

the rare earth ions to order. Near the lower transition temperature, the rare earth atoms order antiferromagnetically.

The values of the effective magnetic moment obtained (Table 1) do not agree with any of the oxidation states of $Cr^{3+}$ ($3d^3$) and $Cr^{4+}$($3d^2$) with effective moments of $2.83\mu_B$ and $3.87\mu_B$ per atom, respectively. In a neutron study, Raju et al. [3] reported the existence of a strong ferromagnetic exchange between the itinerant electrons in the $CrSb_2$ layer in which chromium does not have a definite oxidation state. The $p_{eff}$ obtained for $CeCrSb_3$, $PrCrSb_3$ and $NdCrSb_3$ implies that this an undefined oxidation state of Cr exist for at least the first four members of the series. In the view of weak ferromagnetism, the effective magnetic moment and the saturation magnetic moment can not be consistently described by the same angular momentum quantum number $J$, this behavior has been explained by Moriya [5] in terms of spin fluctuation theory.

The low temperature transition in $RCrSb_3$ with R=Ce, Pr, Nd, is shown in Fig. 2. On one hand, we attribute this to be the transition temperature of RSb phase which was determine to be present in our samples by X-ray diffraction. The values are consistent with that reported by Busch [6] for RSb. On the other hand, Hartjes et al. ascribed this transition to the order of the $R^{3+}$ moment (absent for R=La). In this case, we can conclude from our result that there is a transition in the magnetic structure to a non collinear/canted structure due to antiferromagnetic interaction. The magnetization data for $NdCrSb_3$ (Fig. 4) confirms this conclusion. The non linear variation of the magnetization in external magnetic field is indeed an effect of field induced transition to a collinear magnetic structure. Saturation magnetization is not reached at 5.5 T for all compounds. One can conclude that these compounds are ferromagnets that saturate at fields beyond 5.5 T. It is also possible that the intermetallic compounds with R=Ce, Pr, Nd are itinerant electron ferromagnets, magnetization measurement remains to be done at high magnetic field or other types of measurement to clarify the nature of these compounds.

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