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Magnetic properties of LaCr$_{1-x}$M$_x$Sb$_3$ (M=V, Mn, Fe, Cu, and Al)

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The influence of Cr substitution by various metals (M=V, Mn, Fe, Cu and Al) on the magnetic state of the itinerant intermetallics La(Cr,M)Sb$_3$ was studied by magnetization and magnetic susceptibility measurements up to 55 kG at 5 K and from 4.2 to 400 K, in a magnetic field of 1000 G, respectively. It was found that the Curie temperature (T_C) and magnetization (M) of these compounds depend nonlinearly on the concentration, remaining in the vicinity of the values of T_C and M measured for LaCrSb$_3$. Curie temperatures and magnetization values at 55 kG are suppressed by Mn, Fe, V, and Cu, and have a slight maximum at low Al concentration (about 5%). © *2001 American Institute of Physics.* [DOI: 10.1063/1.1356039]

I. INTRODUCTION

Intermetallic alloys combining a $4f$ metal (R), the source of large magnetocrystalline anisotropy, with a $3d$ transition metal (T), the source of large magnetic exchange coupling, are an interesting class of materials for the study of the basic magnetic behavior of materials having possible technological applications. In addition, much current research in magnetism has turned to bulk materials consisting of layers and chains of atoms exhibiting reduced dimensionality in magnetic and transport properties. Examples of such materials include the high temperature superconducting materials and the layered colossal magnetoresistance materials.[1] Substitution of different elements in these compounds can allow one control of the magnetic aspects of these materials through variations in the interlayer and intra-layer couplings.

Recently, a new class of R-$3d$ intermetallic alloys with the chemical formula RTSb$_3$ (R=La, Ce, Pr, Nd, Sm, Gd, Tb, and Dy; T=Cr and V) and orthorhombic symmetry (space group Pbcm) was discovered.[2,3] These compounds are layered materials consisting of two-dimensional layers and one-dimensional chains of atoms. In these layered materials it is thought that the rare earth metal stabilizes the low-dimensional features such as layers and chains.

RCrSb$_3$ (R=La, Ce, Pr, and Nd) intermetallic compounds show ferromagnetic ordering of the Cr sublattice below about 145 K and antiferromagnetic ordering of the rare earths Ce, Pr, and Nd at lower temperatures.[4] This is an interesting result in light of the fact that chromium itself is an itinerant spin density wave antiferromagnet, and frequently exhibits antiferromagnetic order in intermetallic compounds rather than ferromagnetic behavior. Magnetization measurements made on RCrSb$_3$ with R=Gd, Tb, and Dy showed no magnetic order in the Cr sublattice down to 4.2 K, only a low temperature antiferromagnetic ordering of the rare earth.[4] Previous work on RTSb$_3$ (T=Cr, V) shows that both Cr and V transition metals carry a magnetic moment in these com-

pounds, the moment on Cr corresponding approximately to two unpaired electrons and that on the V atom corresponding to one unpaired electron.[5] However, another study finds that the interatomic distances in the Cr compounds are consistent with a formal Cr oxidation state between 3+ and 4+,[6] suggesting that the magnetism of the transition metal sublattice may not be so simple to understand within the scope of the Heisenberg theory of magnetism (localized magnetic moments). Recent neutron diffraction measurements and band structure calculations show the possibility of the itinerancy of the Cr magnetic subsystem in these compounds.[2] Hence, studies focused on investigating phenomena peculiar to localized or itinerant electrons would provide a meaningful insight in understanding the nature of Cr magnetism in RCrSb$_3$ compounds. One of the possible ways to determine whether the Cr system exhibits itinerant or localized moments is to study the magnetic behavior of RCrSb$_3$ as the result of Cr substitution by another metal. Here we look at the effect of substituting other metals on the Cr site in LaCrSb$_3$. If the atom substituted for Cr has a larger ionic
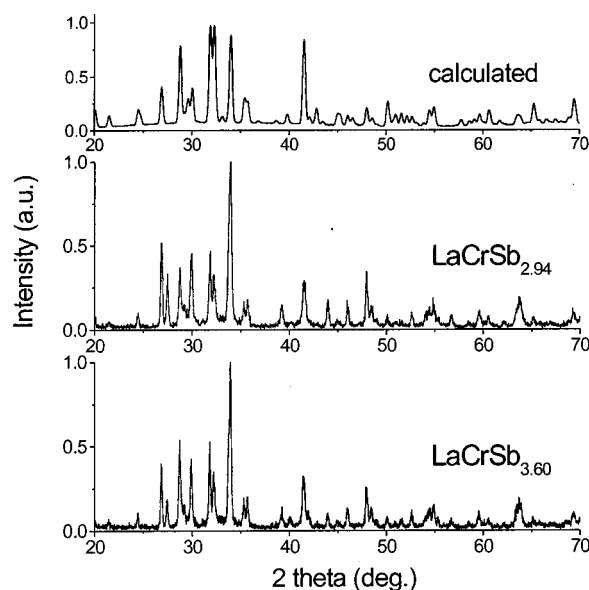

FIG. 1. Comparison of x-ray diffraction data of LaCrSb$_x$ for $x=2.94$ and 3.60 with the calculated pattern for $x=3.00$.

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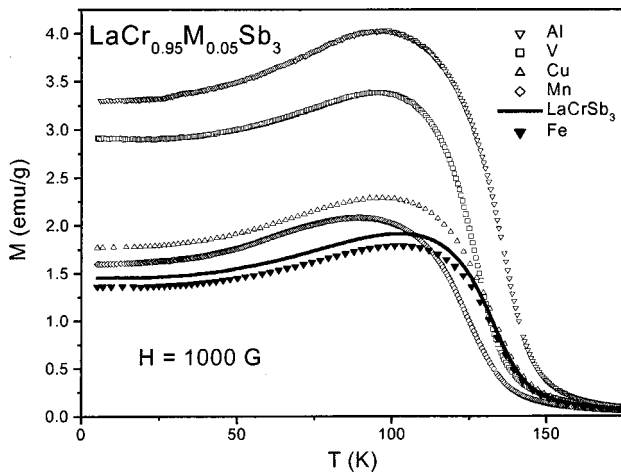FIG. 2. Magnetization as a function of temperature for 5% substitutions of V, Mn, Fe, Cu, and Al. All samples were measured at a field of 1.0 kG.

FIG. 4. Magnetization as a function of temperature in a field of 1 kG for 5% and 10% substitutions of Fe for Cr.

radius then it will tend to expand the lattice, increasing the interatomic distances and possibly distorting the structure, which, in turn, will alter the magnetic exchange interactions. Likewise, a substituent with a smaller ionic radius will contract the lattice, bringing the atoms closer together. Substitutions on the transition metal site will also alter the d-electron concentration, which may also alter the magnetic properties of the system.

II. EXPERIMENTAL DETAILS

Samples of $LaCrSb_3$ with substitutions of 5%, 10%, and 20% V, Mn, Fe, Cu, and Al were prepared. All samples were synthesized by induction melting appropriate amounts of La, Cr, Sb, and the substituent transition metals in an argon atmosphere. X-ray powder diffraction patterns were obtained utilizing Cu $K\alpha$ radiation on a Scintag XDS 2000 diffractometer to determine the structure and phase purity of the alloys. Magnetic measurements from 5 to 400 K and in fields
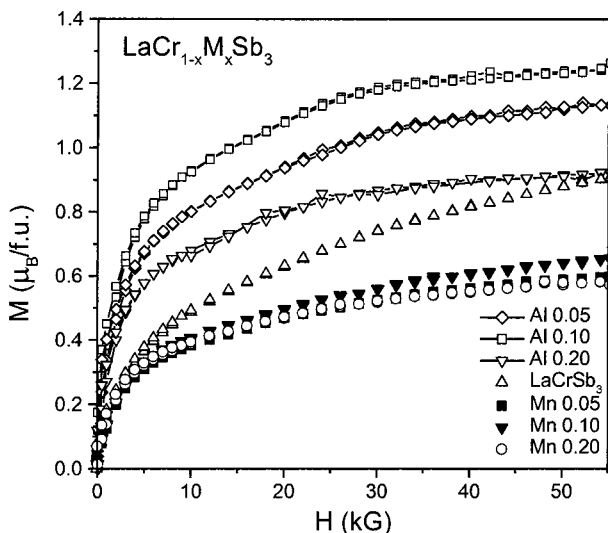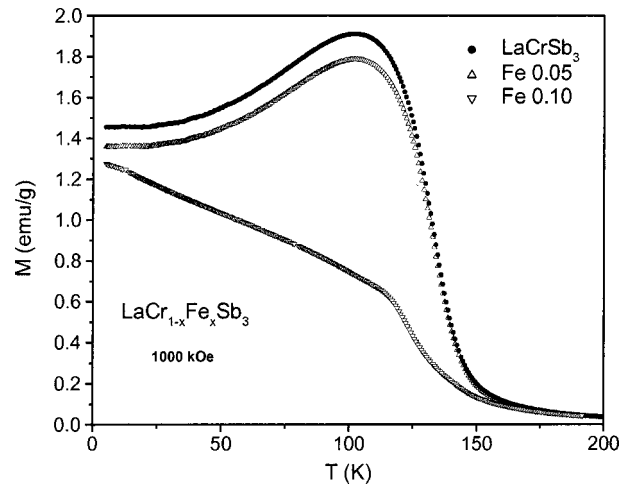
up to 5.5 T were obtained in a Quantum Design superconducting quantum interference device magnetometer.

Since antimony is volatile, and some is lost during sample preparation, we first wanted to know if this factor would cause changes in structure and magnetic properties that would interfere with changes induced by the substituted elements. Initially we prepared a number of samples of $LaCrSb_3$ with starting concentrations of $Sb_{2.88}$, $Sb_{2.94}$, $Sb_{3.4}$, and $Sb_{3.6}$ to determine the effect of excess or deficit Sb on the crystal structure and magnetic properties of the samples. Figure 1 shows the results of our x-ray measurements on some of these samples. Surprisingly, we found that the x-ray data obtained for samples with different concentrations of antimony show that all samples are predominantly of the $LaCrSb_3$ structure, with small amounts of impurities (5%–10%) across the series. Magnetization as a function of temperature was measured for all samples and showed that the Curie temperature remained fairly constant near 130 K. Thus, it appears reasonable that small errors in stoichiometry of the samples will not interfere with our ability to detect changes in physical and magnetic properties of the alloys induced by the substituents. We chose $Sb_{2.94}$ as the starting concentration for our substitution studies since this concentration is close to the value of 2.909 obtained by Brylak and Jeitschko[3] in their structure refinements and it has a lower impurity concentration (about 5%).

FIG. 3. Magnetization measurements at 5 K as a function of field for $LaCr_{1-x}M_xSb_3$ for M=Al and Mn.

TABLE I. $LaCrSb_3$ has $T_c=133$ K and a value of M at 5.5 T and 5 K of 0.91 μ_B/f.u.

Substituents	T_c (K)			M at 5.5 T and 5 K (μ_B/f.u.)		
	5%	10%	20%	5%	10%	20%
V	128	110	108	1.10	1.25	1.10
Mn	124	131	122	0.65	0.60	0.58
Fe	133	123	⋯	0.81	0.80	⋯
Cu	132	130	122	0.98	0.90	0.69
Al	138	134	128	1.13	1.25	0.92

III. RESULTS AND DISCUSSION

Figure 2 presents the effects of a 5% substitution of elements V, Mn, Fe, Cu, and Al on the magnetic ordering temperature of LaCrSb$_3$. It is readily seen that at this concentration none of the elements has a large effect on the ordering temperature of this compound. Al slightly increases the ordering temperature while V and Mn suppress it slightly. In fact, not much difference was noted at 10% and 20% substitutions as well. Both Al and V tend to increase the magnetization at 5.5 T (from 0.91 μ_B/f.u.) for LaCrSb$_3$, while Fe and Mn tend to suppress it. Values of T_C and M at 5.5 T with respect to concentration are given in Table I. We also noted that the effects of substituting small amounts of these other metals for Cr was nonlinear with respect to concentration.

Aluminum was chosen as a substituent since it has a substantially larger metallic radius than Cr and would tend to expand the lattice, thereby possibly weakening the magnetic exchange. Since it has no electrons to contribute to the d band, substituting Al for Cr should change the d band and reduce its electron concentration. It is observed in our data (Table I) that substitution of Al for Cr results in a slight increase of T_C at the 5% level, but a reduction in T_C for subsequent concentrations. However, it is noted that addition of Al increases the magnetization at 5.5 T for all concentrations (Fig. 3), with the greatest value occurring at 10%. We also note that x-ray data for the 20% aluminum sample shows the presence of impurity phases. These may be due to the larger Al size destabilizing the Pbcm structure of this compound.

Manganese has a slightly smaller metallic radius than Cr and often orders antiferromagnetically, therefore, though it may tend to contract the lattice, bringing the magnetic ions closer together, it may also weaken the magnetic coupling by tending to align antiferromagnetically with the Cr ions. Our measurements show that substitution of Mn for Cr in LaCrSb$_3$ results in both a reduction in T_C (Table I) and suppression of the magnetization at 5.5 T (Fig. 3).

Vanadium has a slightly larger metallic radius than Cr and is normally nonmagnetic. The isostructural compound LaVSb$_3$ shows no magnetic ordering of the V sublattice down to 2 K, despite the fact that vanadium in LaVSb$_3$ is observed to have an effective paramagnetic moment of 1.53 μ_B, consistent with $p_{eff} = 1.73 \mu_B$ expected for an ion with one uncompensated spin.[5] Additions of V to LaCrSb$_3$ tend to monotonically suppress the Curie temperature (down to 108 K for 20% V) while increasing the high field magnetization.

The substitution of Cu, which has nearly the same metallic radius as Cr and is normally nonmagnetic, has little effect on the magnetic properties of LaCrSb$_3$ at small concentrations. With increasing concentration we observe a slight reduction in both T_C and magnetization.

Iron is smaller than Cr and is normally a very good ferromagnet, thus it was thought that it might serve to enhance the ferromagnetic interactions between the Cr ions. However, substitution of Fe reduced both T_C and the magnetization at 5.5 T. Even though substitutions of V decrease T_C more rapidly than Fe, the character of the transition remains the same. Figure 4 shows that with only a 10% substitution of Fe for Cr the shape of the magnetization curve at low temperature changes dramatically.

IV. SUMMARY

The study of the effect of substitution of Cr by small amounts (up to 20%) of other metals, V, Mn, Fe, Cu, and Al, in LaCrSb$_3$ shows that changing the character of the ion on the Cr sites has little effect on the magnetic properties of this compound. The ferromagnetic order exhibited by the Cr lattice was found to be fairly robust and resistant to small changes in stoichiometry, d-band occupation, and magnetic character of the substituted metal. This behavior cannot be understood within the scope of the localized model of magnetism: the Curie temperature and magnetization of compounds with localized stable spins are directly proportional to the magnetic ion concentration. On the other hand, these characteristics can be essentially nonlinear in itinerant magnets, since the replacing ions can affect in a different way the energy dependence of the density of d-electron states near the Fermi level.[7,8] It is therefore suggested that the Fermi level is placed near the maximum of the density of states in RCrSb$_3$. In that case any density of states variation results in a decrease of T_C. It will be interesting now to extend our experiments to higher concentrations of several of these materials. Since vanadium forms an isostructural compound it may be especially instructive to observe the magnetic–nonmagnetic crossover as V is substituted for Cr.

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