The RAgSb$_2$ ($R$=rare earth) series of compounds crystal-
lizes in a simple tetragonal ZrCuSi$_2$-type structure (P4/nmm,
No. 129). The sheetlike layers of Sb, Ag, and R-Sb are
stacked along the crystallographic c-axis. This structure
gives rise to a single, unique crystallographic site of tetra-
gonal point symmetry for the rare earth and to anisotropic
conductivity, that is much higher within the basal plane than
along the c-axis. Members of the family show rich and com-
plex electronic and magnetic properties ranging from aniso-
tropic, ferromagnetic, Kondo-lattice behavior in CeAgSb$_2$ to
intricate, albeit tractable, low-temperature, crystalline elec-
tric field (CEF) governed metamagnetism in compounds with
$R$=heavy rare earths. This family has recently received in-
creased attention due to the successful growth of high
quality single crystals that are suitable for detailed, aniso-
tropic thermodynamic and transport measurements.

YAgSb$_2$ and LaAgSb$_2$ are nonmagnetic, but still highly
anisotropic (structurally), members of the series. Whereas
YAgSb$_2$ has characteristics of a normal metal with a multi-
sheet Fermi surface (FS) and no apparent anomalies in its
thermodynamic or transport properties, LaAgSb$_2$, being
similar to YAgSb$_2$ in its overall behavior, has a striking fea-
ture in its temperature dependent resistivity, $\rho(T)$, at $T_1$
=210 K and a much smaller anomaly at $T_2 \approx 185$ K. Cor-
responding features were also observed in the magnetic
susceptibility. The feature in $\rho(T)$ was tentatively inter-
preted as related to a density wave transition. Temperature
dependent lattice parameters measurements left the origin of
the anomalies somewhat ambiguous. Recently, a careful
x-ray scattering study revealed that both features are the
signatures of charge-density-wave (CDW) orderings with the
higher temperature one marking a development of periodic
charge/lattice modulation along the $a$-axis with the wave
vector $\tau_1 \approx 0.026(2\pi/a)$ and the lower temperature one
indicating an additional CDW ordering along the $c$-axis with
the wave vector $\tau_2 \approx 0.16(2\pi/c)$. Both CDW orderings were
shown to be consistent with the enhanced nesting in the
different parts of the LaAgSb$_2$ Fermi surface: for the higher
temperature CDW transition the nesting occurs in the $ab$
plane, on the large, square-cylinder-shaped FS part (band 3
in the notation of Ref. 4), for the lower temperature CDW
transition the relevant nesting is along the $k$, direction and is
related to the three-dimensional pillow-like-shaped FS part
(band 1 in Ref. 4) (see Ref. 7 for further details).

Since the CDW ground state typically develops as a con-
sequence of electron-phonon interactions and Fermi sur-
face nesting (often in low dimensional metals), it is expected
to be sensitive to any (anisotropic) changes in the lattice
parameters of the material. Two ways to alter the lattice pa-
rameters of LaAgSb$_2$ are readily available: (i) pressure and
(ii) chemical substitution. In noncubic materials application
of hydrostatic pressure often results in anisotropic, relative
changes in the lattice parameters that are nominally continu-
ous and well controlled. Isoelectronic substitutions also in-
duce changes in lattice parameters that can be of both signs
(“positive” and “negative” chemical pressure) depending on
the relative ionic sizes. In complex crystals “local” structural
changes do not necessarily scale with the global changes in
lattice parameters, additionally, doping induces some disor-
der, so the comparison between physical and chemical pres-
sure may be not straightforward.

In this work we compare steric effects caused by pressure
and substitution on the temperature of the CDW formation in
LaAgSb$_2$ in the hope of finding a single structural parameter
that can be used for both perturbations. We will concentrate
on the higher temperature CDW transition, since it has a very
pronounced feature in the in-plane resistance measurements.
Here we will consider only rare earth site substitutions: they
are isoelectronic, and are tolerated by the structure for a
number of rare earths with no apparent solubility limit. To
make a comparison between chemical and physical pressure,
the anisotropic compressibility of LaAgSb$_2$ was independ-
ently measured.

High quality platelike La$_{1-x}$R$_x$AgSb$_2$ single crystals were
solution-grown from Sb rich self-flux (see Refs. 3 and 4
for further details). The crystals had typical dimensions of
5 × 5 × 2 mm³ with the c-axis perpendicular to the plates and clearly seen facets. The samples chosen for this study were pure LaAgSb₂, La₁₋ₓGdₓAgSb₂ (x = 0.05, 0.1, 0.15, 0.2), La₁₋ₓCeₓAgSb₂ (x = 0.05, 0.1, 0.15, 0.2), La₁₋ₓYₓAgSb₂ (x = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3), and La₀.₉Nd₀.₁AgSb₂. Room temperature ambient pressure powder x-ray diffraction measurements were performed in a Philips diffractometer using Cu Kα radiation. Lattice parameters were obtained from the Rietveld fits of the x-ray spectra using the Rietica software. Magnetization measurements (1.8 K ≤ T ≤ 350 K, H = 55 kOe) were performed in a Quantum Design MPMS-5 SQUID magnetometer. The crystals used for resistance measurements were cut in approximately bar shape with typical dimensions, 2–3 mm length, 0.7–1 mm width, 0.3–0.7 mm thickness. Resistance measurements were carried out using a standard four-probe ac technique (f = 16 Hz, I = 1–3 mA) with platinum leads attached to the sample using Epotek H2O silver epoxy so that current was flowing in the (ab) plane, approximately in the [100] direction. It must be noted that for zero applied magnetic field measurements (in the Ohmic regime) the in-basal-plane resistivity for tetragonal crystals does not depend on the in-plane direction of the current (see, e.g., Ref. 14). For ambient pressure measurements a Quantum Design PPMS-9 with the ACT option was used. Resistance measurements were performed in an Oxford Instruments cryostat with a variable temperature insert at the temperature calibration for this cell.15 The CDW transition temperature for La₁₋ₓAgSb₂ at ambient pressure and for LaAgSb₂, under pressure was determined from the sharp minimum in the inverse susceptibility is consistent with the nominal concentration x cited in the chemical formula. Since the size of Gd³⁺ ion is close to the size of Y³⁺ ion, and for the former nominal and estimated value of x is very similar, we can be confident that the same will hold for the latter. Whereas this approach suffers when substantially nonlinear a(x) or c(x) behavior is observed, it has an advantage of avoiding error bars usually for powder XRD taken on laboratory diffractometer and keeping, at least semiquantitatively, the correct lanthanide contraction trends. A study of a wider range of substitution for various members of the RAgSb₂ series provides this simplifying assumption.22

Relative changes in the lattice parameters and unit cell volume under pressure are shown in Fig. 1. From these data the values for linear compressibilities are β₉₀ = 0.29(1) × 10⁻³ kbar⁻¹, β₀ = 0.81(1) × 10⁻³ kbar⁻¹ and the bulk (SRM 674). A powdered sample (ground single crystals) of LaAgSb₂ was loaded into the DAC at ambient pressure and room temperature along with a few small ruby chips. The sample chamber is provided by a 200 μm hole formed in the center of a 250 μm thick stainless steel gasket. A mixture of 16:3:1 by volume of methanol:ethanol:water was used as a pressure transmission fluid. The pressure at the sample was measured by detecting the shift in the R₁ emission line of the included ruby chips. Structural models were refined using the Rietveld method.19 Bulk moduli and pressure derivatives were calculated by fitting the normalized volumes to a third-order Birch-Murnaghan equation of state,19

\[ P = \frac{3}{2} B₀ \left( \frac{V}{V₀} \right)^{-7/3} - \frac{3}{4} \left( B₀' - 4 \right) \left( \frac{V}{V₀} \right)^{-2/3} - 1 \]

(where B₀ is a bulk modulus and B₀' is its pressure derivative) and no constraints or weights were used in the fit.

Powder x-ray diffraction confirmed that all the samples were single phase with the lattice parameters for pure LaAgSb₂ being consistent with the literature data and lattice parameters for the doped samples following the expected lanthanide contraction trend, within the error bars of the measurements, observed for different rare earths in pure RₐGₐSb₂.1,2,20,21 It should be noted that the change in the lattice parameters between the pure LaAgSb₂ and the La₁₋ₓRₓAgSb₂ (x = 0.3) used in this work is rather small (<1 %). Given this small change, in the analysis of the relations between the CDW transition temperature and structural parameters of the La₁₋ₓRₓAgSb₂ series below we will use linear interpolation between the end-members' of the series for each rare earth dopant using the nominal value of x. Whereas the evolution of the long range order and formation of the spin-glass state in different La₁₋ₓAgSb₂ (x ≠ 0, R ≠ Y) is the subject of a separate study,22 the relevant information for this work from the magnetization measurements is that the concentration of dopant, x, inferred from the effective magnetic moment estimated from the linear part of the inverse susceptibility is consistent with the nominal concentration x cited in the chemical formula. Since the size of Gd³⁺ ion is close to the size of Y³⁺ ion, and for the former nominal and estimated value of x are very similar, we can be confident that the same will hold for the latter. Whereas this approach suffers when substantially nonlinear a(x) or c(x) behavior is observed, it has an advantage of avoiding error bars usual for powder XRD taken on laboratory diffractometer and keeping, at least semiquantitatively, the correct lanthanide contraction trends. A study of a wider range of substitution for various members of the RAgSb₂ series supports this simplifying assumption.22

In situ, high pressure, synchrotron x-ray powder diffraction experiments were performed using a diamond anvil cell (DAC) at the X7A beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Details regarding the experimental setup are given elsewhere.16 The primary white beam from the bending magnet is focused in the horizontal plane by a triangular, asymmetrically cut Si (111) monochromator bent to a cylindrical curvature by applying a load to the crystal tip, resulting in microfocused (~200 μm) monochromatic x-ray radiation with a wavelength near 0.7 Å. A tungsten wire crosshair was positioned at the center of the goniometer circle and subsequently the position of the incident beam was adjusted to the crosshair. A gas-proportional position-sensitive detector was stepped in 0.25° intervals over the angular range of 5°–30° with counting times of 30 s per step. The wavelength of the incident beam [0.6638(1) Å], PSD zero channel and PSD degrees/channel were determined from a CeO₂ standard.
modulus and its derivative are $B_0 = 0.74(3)$ Mbar, $B'_0 = 4.8(15)$. The linear compressibilities are anisotropic with $\beta_{0,0}$ being almost three times higher than $\beta_{0,1}$. The obtained bulk modulus and its derivative are similar in value to those obtained for a few intermetallics, e.g., CeTIn$_5$, PuTGa$_5$, and Ce$_2$TIn$_6$,$^{23,24}$ however the linear compressibilities of LaAgSb$_2$ are significantly more anisotropic.

The temperature-dependent resistivities of LaAgSb$_2$ taken at different pressures up to 7.5 kbar are shown in Fig. 2. Such moderate pressures decrease of $T_{\text{CDW}}$ by more than 20 K and also apparently very slight (less than 10% between 2.4 and 7.5 kbar) decrease of the residual resistivity ratio, $\text{RRR} = \rho(300 \text{ K}) / \rho(2 \text{ K})$. The pressure dependence of the CDW transition temperature is linear in this pressure range with the pressure derivative $dT_{\text{CDW}}/dP = -4.3 \pm 0.1$ K/kbar.

The temperature dependent resistivity for the La$_{1-x}$Gd$_x$AgSb$_2$ series with $0 \leq x \leq 0.2$ is shown in Fig. 3. The general shape of the $\rho(T)$ curves remains the same for all levels of substitution shown. Residual resistivity ratio decreases from ~58.5 for $x=0$ to ~9.4 for $x=0.2$. The feature associated with the CDW moves down in temperature (dropping by ~100 K for $x=0.2$) with respect to pure LaAgSb$_2$ (see inset). This feature cannot be unambiguously seen for higher available Gd concentrations. Apparently the decrease of $T_{\text{CDW}}$ is very steep above $x=0.2$ or the extreme broadening of the feature prevents us from detecting it.

Very similar, albeit somewhat slower, evolution of the resistivity data is observed for the La$_{1-x}$Y$_x$AgSb$_2$ series ($0 \leq x \leq 0.3$) (see Fig. 4) and for La$_{0.9}$Nd$_{0.1}$AgSb$_2$ (Fig. 5). For La$_{1-x}$Y$_x$AgSb$_2$ $T_{\text{CDW}}$ monotonically decreases down to ~75 K for $x=0.3$ ($\text{RRR} \sim 8$) but at this point even the $(dp/dT)[1/\rho(300 \text{ K})]$ data is growing indistinct; for La$_{0.9}$Nd$_{0.1}$AgSb$_2$ $T_{\text{CDW}} \sim 176$ K, $\text{RRR} \sim 8$.

In the La$_{1-x}$Ce$_x$AgSb$_2$ series already a 5% substitution of Ce changes the functional dependence of $\rho(T)$ (Fig. 6). For $x=0.05$ and 0.1 an upturn in the low temperature resistivity associated with a single-ion Kondo effect is clearly seen, for $x=0.15$ and 0.2, in addition to the upturn, a loss of spin disorder associated with a long range magnetic order can be seen. While the complex evolution of the ground state in the La$_{1-x}$Ce$_x$AgSb$_2$ series will be discussed elsewhere,$^{22}$ here we mention that $T_{\text{CDW}}$ in this series decreases with an increase of Ce substitution and $\text{RRR}$ decreases as well, although the comparison with the $\text{RRR}$ change in the other series under study is ambiguous due to the additional possible contributions to the $\rho(T)$ in the La$_{1-x}$Ce$_x$AgSb$_2$ series from the hybridization of the Ce 4f levels.

Plots of the CDW transition temperature as a function of...
FIG. 4. Normalized temperature dependent resistivity for La\(_{1-x}\)Y\(_x\)AgSb\(_2\), \(x=0, 0.05, 0.1, 0.15, 0.2, 0.25, \) and 0.3 (from bottom to top). Curves are shifted along vertical axis for clarity. Arrows mark CDW transitions. Inset, derivatives \((d\rho/dT)/(1/\rho(300 K))\) for \(x=0, 0.1, 0.2, \) and 0.3. * marks inferred \(T_{CDW}\) values.

The different crystallographic parameters: \(a\) - and \(c\)-lattice parameters, unit cell volume, \(V\), and ratio \(c/a\) are shown in Fig. 7. (Note that scattering of data for the La\(_{1-x}\)Y\(_x\)AgSb\(_2\) series is higher than for other rare earth substitutions, the possible reason being the absence of independent evaluation of the Y concentration—see above for details.) No universal behavior of the CDW transition temperature is observed for different substitutions and for pressure when \(T_{CDW}\) is plotted vs either lattice parameters or the unit cell volume [Figs. 7(a)–7(c)]. However, the \(T_{CDW}\) vs \(c/a\) plot [Fig. 7(d)] clearly shows all data falling approximately on one of two well-separated lines: a rather steep line with all substitutions data and another line, with a more moderate slope, that is defined by the pressure data. It is not surprising to have \(c/a\) as a salient parameter for pressure data: the details of the shape and local curvature of the cylindrical FS parts (such as one that defines nesting vectors relevant for the higher temperature CDW transition studied here) are often very sensitive to the dimensionality of the material of which \(c/a\) is an approximate caliper. The evolution of the “dimensionality” of the material as evaluated from the \(c/a\) ratio appears to be an important parameter that controls \(T_{CDW}\), but not the only one. Whereas the hydrostatic pressure is a “clean” way to change the lattice parameters and often the \(c/a\) ratio, chemical pressure (doping), in addition to steric changes, always introduces some disorder. The effect of impurities (disorder) on the CDW transition was studied for several decades (see, e.g., Ref. 25 and reviews\(^{10,11}\)). Two kinds of effects are expected in the case of an incommensurate CDW (which the higher transition in LaAgSb\(_2\) is an example of):\(^7\) lowering of the transition temperature and broadening of the transition.\(^{25}\) Both of these effects are observed in the La\(_{1-x}\)R\(_x\)AgSb\(_2\) series at ambient pressure (see e.g., Fig. 4 for La\(_{1-x}\)Y\(_x\)AgSb\(_2\)). However Fig. 7(d) suggests that disorder caused by the rare-earth substitution is the dominant factor in decrease of \(T_{DW}\). For La\(_{1-x}\)R\(_x\)AgSb\(_2\) materials at the ambient pressure. Therefore it is not surprising that the data for all substitutions fall approximately on the same line on \(T_{CDW}\) vs \(c/a\) plot [Fig. 7(d)] since the \(c/a\) ratios for the end-compounds: GdAgSb\(_2\), YAgSb\(_2\), CeAgSb\(_2\), and NdAgSb\(_2\) and therefore for La\(_{1-x}\)R\(_x\)AgSb\(_2\) samples with the same \(x\) are very close to each other.\(^{1,2,22}\)

In summary, data in Fig. 7 lead to the conclusion that the evolution of the CDW transition temperature in LaAgSb\(_2\) under pressure and with the rare-earth doping can be described as a combination of two effects: change of the structural anisotropy and disorder, the former being dominant in pressure experiments and the latter prevailing in the case of doping.
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14 D. R. Lovett, Tensor Properties of Crystals (Institute of Physics, Bristol, Philadelphia, 1989).