Cubic-to-Tetragonal Transformation and Susceptibility in $LaAg_xIn_{1-x}$ Alloys*

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The magnetic susceptibility $\chi(x,T)$ of the pseudobinary intermetallic compound $LaAg_xIn_{1-x}$ is given for temperatures T between 20 and 250 K with x between 1.0 and 0.15. For x between 0.9 and 0.6, χ is very anomalous, rising strongly as the samples are cooled until a temperature $T_M(x)$ is reached where a cubic-to-tetragonal crystallographic transformation is found to occur and the susceptibility drops to a much lower value. The transformation is shown to arise from a band Jahn-Teller effect. The behavior of $\chi(x,T)$ as well as $T_M(x)$ can be described quantitatively over a broad range of x assuming that the Fermi energy of LaAg lies closely below a high peak in the density of states which originates from the e_g states of La. This peak becomes gradually populated as the electron concentration is increased by replacing Ag by In.

I. INTRODUCTION

The characteristics of valence and conduction electrons are of fundamental importance for the structure of metals and alloys[1,2] and the relationship between electronic properties and crystal structure has assumed a strong theoretical posture within the formalism of pseudopotential theory.[3] Unfortunately, pseudopotential theory relies rather heavily on the wide-band properties of electrons; therefore, it works best for s-p bonded metals, but poorly for narrow bands.

Recently, work on A-15 intermetallic compounds[4] (high-temperature superconductors which transform structurally from a cubic to a tetragonal phase in the normal state) shows that the narrow d bands of the transition elements can be all important in determining the stable crystallographic structure.[5-10] Since effects of a tetragonal deformation on the electronic d bands are presumably too small to be resolved in band-structure calculations, special models must be developed to describe the experimental observations. One rather successful approach for the A-15 compounds is the band analog of the Jahn-Teller effect due to Labbé and Friedel.[5-7]

The essential idea is that a lattice deformation partially removes the degeneracy of d subbands which may lie in the vicinity of the Fermi level, causing a repopulation of the various subbands, and resulting in a lowering of the crystal-free energy. Because the A-15 compounds possess linear chains of transition-metal ions, the theory of Labbé and Friedel employs a one-dimensional density of states for the d subbands. Although their model seems to depend heavily on the one dimensionality, Cohen *et al.*[8] and Rehwald *et al.*[9] were able to explain the elastic and magnetic properties of the A-15 compound Nb_3Sn by simply assuming a pronounced steplike increase in the density of states just below the Fermi edge. An essential result of the Jahn-Teller model of Labbé and Friedel is the strong dependence of the lattice deformation temperature on the population of states in a high-density-of-states region. Unfortunately, a test of the model by a systematic variation of carrier concentration seems to be impossible in the A-15 compounds for chemical reasons.

Recently,[11] a cubic-to-tetragonal lattice transformation was discovered in the pseudobinary solid solution of the intermetallic compounds LaAg and LaIn. This is a particularly simple system possessing the cubic CsCl structure at room temperature. Although the compounds show no superconductivity above 2 K, this system is of interest in relation to the A-15 compounds because one observes here a similar crystallographic transition without chainlike atom arrangements, and one can study the dependence of the transition on the electron concentration over a wide concentration range.

In the first part of this paper we present experimental results on the magnetic susceptibility for the series $LaAg_xIn_{1-x}$. From these measurements the temperature T_M at which the lattice instability occurs is obtained as a function of x. Over the concentration range $0.6 \leq x \leq 0.9$ our susceptibility curves are similar to that obtained for the A-15 compound Nb_3Sn.[9] Furthermore, the theoretical prediction of the concentration dependence of $T_M(x)$ based on the Labbé-Friedel model for the A-15 compounds has the general features of that deduced from our measurements. Therefore, in the second part of the paper we attempt a theoretical interpretation of the experimental data adapting the basic ideas of Labbé and Friedel to our three-dimensional bands using an extension of the model employed by Cohen *et al.*[8] and Rehwald *et al.*[9] For pure LaAg, which remains cubic at low temperatures, the Fermi energy is assumed to be located directly below a pronounced rectangular peak in the density of states. [This assumption is

to a certain extent justified by band-structure calculations performed on YCu [12] which show that such a peak may result in the CsCl-type compounds from the narrow, doubly degenerate e_g (Γ_{12}) states of the La ions in their cubic environment.] In a tetragonal environment this peak will be distorted, and the situation is described through a deformation potential. Presuming that the Fermi energy increases with In concentration and that the general features of the density-of-states

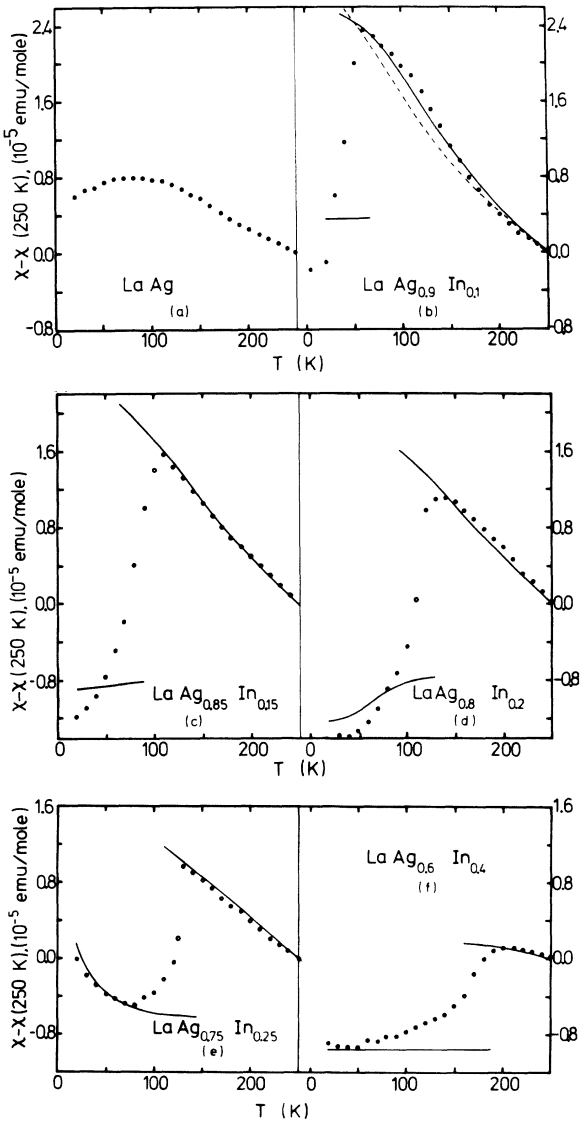

FIG. 1. Magnetic susceptibility of $LaAg_xIn_{1-x}$ in the concentration range $0.6 \leq x \leq 1.0$. The susceptibility is shown relative to its value at $T = 250$ K, and the solid lines are theoretical fits using parameter values given in Table I. The dashed line in Fig. 1(b) is a best fit with a slightly smaller Fermi energy than that assumed for the solid line, and is used to demonstrate the sensitivity of the fits to this quantity.

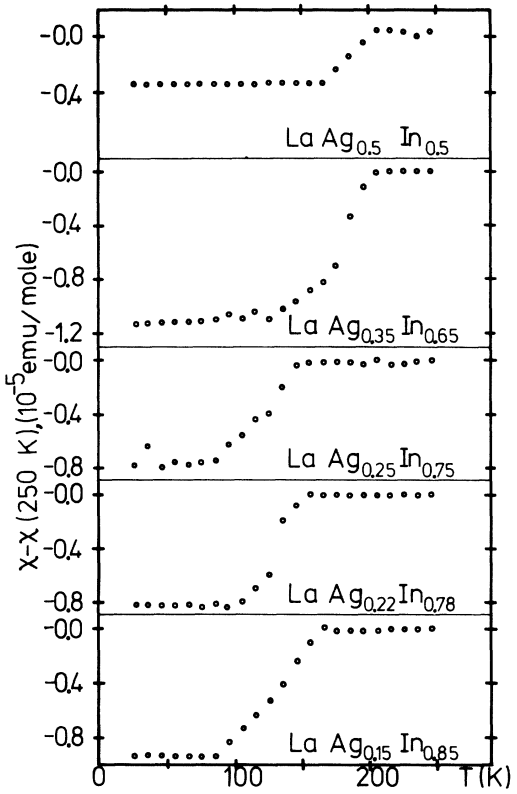

FIG. 2. Magnetic susceptibility of $LaAg_xIn_{1-x}$ in the concentration range $0.15 \leq x \leq 0.5$. The susceptibility is shown relative to its value at $T = 250$ K.

structure are preserved as the In concentration is increased, we obtain a good description of the concentration dependence of the transformation temperature $T_M(x)$ and the susceptibility data over a broad range of x.

II. EXPERIMENTAL RESULTS

Polycrystalline samples of the pseudobinary intermetallic compound $LaAg_xIn_{1-x}$ were prepared from stoichiometric quantities of La, Ag, and In pieces by melting several times in a pure argon arc furnace. The compounds were found to have the cubic CsCl structure at room temperature, and the x dependence of the residual resistivities indicates that indium replaces silver at random. [11]

The magnetic susceptibility was measured in a Faraday balance for temperatures between 4 and 300 K in cooling runs only. The data were corrected for paramagnetic impurities (a few ppm of Ce in La) by subtracting out the corresponding Curie susceptibility. The corrected susceptibility of $LaAg_xIn_{1-x}$, Figs. 1–3, has its largest inaccuracy at low temperatures ($T < 40$ K), where the Ce susceptibility becomes large.

The interesting features of the experimental susceptibility are the strong rise in the susceptibility with decreasing temperature (Fig. 1) and the appearance of a "knee" around the crystallographic transformation temperature T_M (Figs. 1 and 2).[13] Resistivity measurements[11] in $LaAg_xIn_{1-x}$ give a hysteresis in cooling and warming runs centered around the same temperature T_M. The width of this hysteresis could be reduced by annealing, and the temperatures T_M obtained this way by both resistivity and susceptibility measurements are shown as a function of x in Fig. 4, the "error bars" giving the approximate widths of the hysteresis.

Detailed x-ray analysis[11] at temperatures below T_M reveals a tetragonally deformed CsCl structure. The reflections can be indexed by assuming a tetragonal unit cell consisting of eight deformed CsCl cells. Figure 5 compares the lattice constants of the cubic and the tetragonal structure. For a better comparison one-half of the tetragonal lattice constants are plotted.

If the theoretical assumptions made in this paper are correct, one should expect similar phase transformations in a large number of other rare-earth pseudobinary CsCl compounds at isoelectronic compositions. Indeed, a phase transition has been found in LaCd at $T_M = 62$ K, which is only about one-third of the transition temperature found in the isoelectronic composition $LaAg_{0.5}In_{0.5}$. It is, however, to be expected that the transition depends on the ionic size of the constituents. Accordingly, we find *no* transition in YAg_xIn_{1-x} nor in $GdAg_xIn_{1-x}$, but we do find a transition in $CeAg_xIn_{1-x}$, at temperatures comparable with those in $LaAg_xIn_{1-x}$.[14]

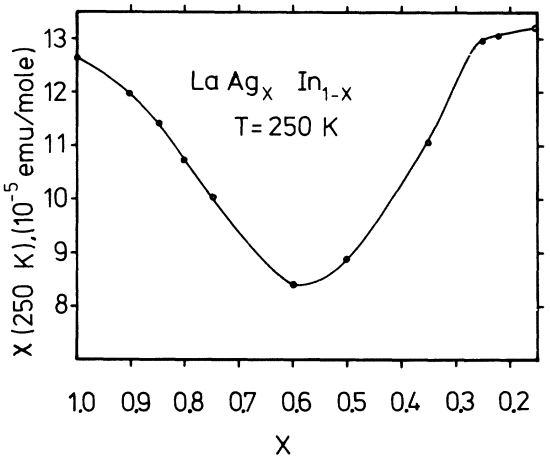

FIG. 3. Absolute magnitude of the magnetic susceptibility of $LaAg_xIn_{1-x}$ at $T = 250$ K as a function of x.

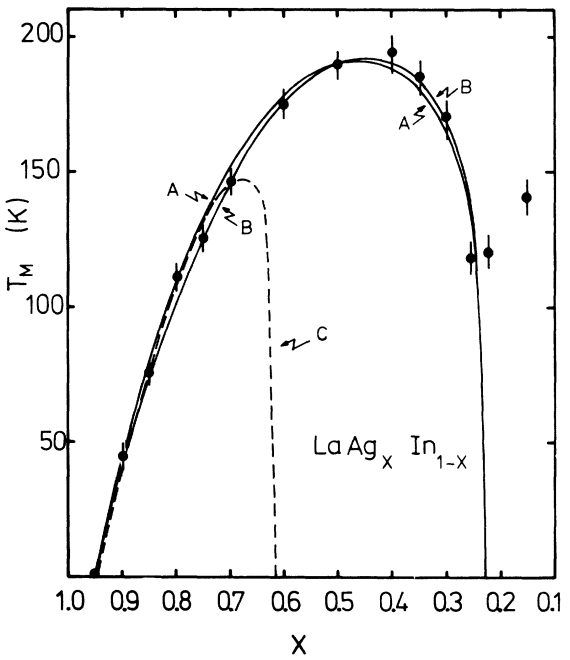

FIG. 4. Crystallographic transformation temperature T_M as a function of x. The curves labeled A, B, and C are theoretical fits obtained with different sets of parameter values given in Table III.

III. THEORY

A good picture of the electronic bands of LaAg and LaIn would be very helpful in understanding the crystallographic transformation and the anomalous behavior of the susceptibility. Although the bands of these compounds have not been computed, there exists a recent APW calculation of YCu[12] which is isostructural to LaAg but has the main quantum numbers reduced by 1. Hence similarities in the general character of the bands in both compounds might be expected.

Of particular interest in the YCu bands is the position of the Fermi energy, which lies within a rather wide band of mixed s-d character, directly below a sharp spike in the density of states. This sharp structure originates from a very flat portion of the twofold orbitally degenerate e_g (Γ_{12}) band of Y d states. We assume that the LaAg conduction bands show the same feature.[15]

It is plausible that the e_g bands formed from the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ states will be very sensitive to tetragonal distortions, for example, on expansion of the lattice along the z axis, with corresponding compressions along the x and y axes. Under such a distortion, the band of the $d_{x^2-y^2}$ states is broadened owing to greater overlap of the electronic wave functions, whereas the band of the $d_{3z^2-r^2}$ states is narrowed. Also, the centers of gravity

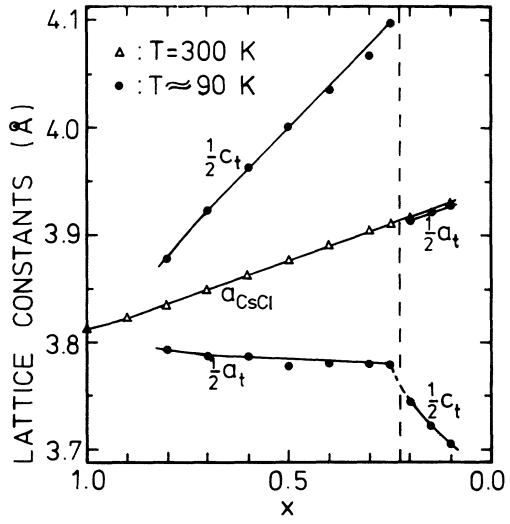

FIG. 5. Lattice constants of $LaAg_xIn_{1-x}$ at two temperatures below and above T_M. The cubic-phase lattice constant is a_{CsCl}, the tetragonal-phase lattice constants are a_t and c_t.

of the two subbands will, in general, shift since a tetragonal crystal field lifts the orbital degeneracy of the e_g states. Under circumstances where the Fermi energy lies in the vicinity of these deforming bands, a repopulation of the states occurs which may result in a lower free energy for the crystal. In this case a spontaneous transformation to the tetragonal phase occurs (very much like a Jahn-Teller effect), with corresponding anomalies in the electronic transport and response coefficients.

To render the problem workable, we describe the band structure of cubic LaAg in the vicinity of the Fermi energy with the simple density of states model[8] shown in the lower portion of Fig. 6. The density-of-states spike due to the e_g bands of La is approximated by a rectangle of height N_0 and width E_0, which is superimposed on a broad s-d conduction band of width $2E_s$ and relative height αN_0.

Under a tetragonal distortion, we assume the band widths E_1 and E_2 due to the states $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, respectively, become

$$E_1 = E_0(1 + U_1\epsilon)\,, \tag{1}$$

$$E_2 = E_0(1 - U_2\epsilon)\,, \tag{2}$$

where U_1 and U_2 are (except for a numerical factor) positive deformation potentials and ϵ is the strain parameter which is larger than zero if the ratio of the lattice constants c/a is larger than 1, and $\epsilon < 0$ if $c/a < 1$.

For simplicity we assume

$$U_1 = U_2 = 2U\,. \tag{3}$$

Then requiring that the total number of states in each subband be the same in the cubic and tetragonal phases, we obtain for the partial density of states

$$N_1(E, \epsilon) = \tfrac{1}{2}N_0[1 - 2U\epsilon/E_0 + 4(U\epsilon/E_0)^2] \tag{4}$$

if the energy E is in the interval $-\epsilon U \leq E \leq (E_0 + \epsilon U)$, and

$$N_2(E, \epsilon) = \tfrac{1}{2}N_0[1 + 2U\epsilon/E_0 + 4(U\epsilon/E_0)^2] \tag{5}$$

if $\epsilon U \leq E \leq (E_0 - \epsilon U)$, corresponding to the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states, respectively.

The total density of states

$$N = \alpha N_0 + N_1 + N_2$$

is shown for $U\epsilon/E_0 = \frac{1}{10}$ in the upper portion of Fig. 6. We ignore any displacement of the center of gravity of the bands due to the tetragonal crystal-field splitting, although this may not be too good an approximation. Also, the background density of states is assumed to be unaffected by the strain.

Having constructed a plausible model for the density of states of LaAg near the Fermi edge, we make the rather drastic assumption that this structure remains intact as indium is alloyed. It should be emphasized that this is not an assumption of rigid bands (which would be an extremely poor one since Ag and In possess valence electrons of different symmetry character); but rather

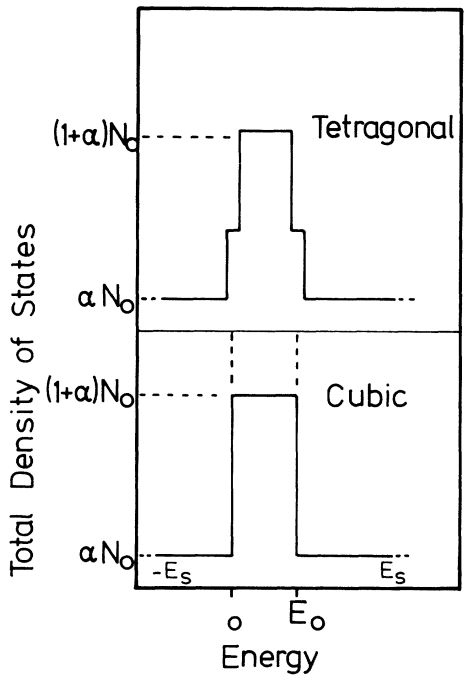

FIG. 6. Model of the total electronic density of states used in the theoretical interpretation of the data.

we assume only that the shape and position of the narrow density-of-states peak produced by the e_g states of La is unaltered by the replacement of Ag by In. The main effect of this replacement is to cause the Fermi energy, which for pure LaAg is assumed to lie directly below the high density-of-states peak, to shift gradually into the peak. The tendency for the Fermi level to rise is due to the fact that In possesses two more valence electrons than Ag. A surprisingly good explanation of the experimental observations is obtained up to moderately high In concentrations using this simple picture of the electronic structure of the alloy.

We begin by assuming that the free energy F of the crystal may be written as a sum of two additive parts

$$F = F_0 + F_d \ . \tag{6}$$

The contribution from the d electron states of La is contained in F_d. The contributions of all other electrons are lumped into F_0.

Treating the electron-electron intra-atomic Coulomb interaction in the Hartree-Fock approximation[16] neglecting interband mixing, we easily obtain the following expression of F_d in the presence of a weak applied magnetic field $\vec{H}$:

$$F_d = \mu Q_d - \frac{kT}{2}\sum_{j,\sigma}\int_{-\infty}^{\infty} N_j(E,\epsilon) \times \ln\left[1+\exp\left(-\frac{E+In_{j,-\sigma}+\sigma\mu_B H-\mu}{kT}\right)\right]dE - \sum_j In_{j\uparrow}n_{j\downarrow} \ . \tag{7}$$

Here μ is the chemical potential, Q_d the total density of d electrons in the e_g subband, k the Boltzmann's constant, T the temperature, $N_j(E,\epsilon)$ the density of states in the jth subband [$j=1$ or 2; cf. Eqs. (4) and (5)], I the Coulomb interaction constant (normally denoted by U in Hubbard theories[16]), and $n_{j,\sigma}$ is the average density of electrons in the jth subband of spin σ($\sigma = \downarrow$ or $\uparrow$), which is given by

$$n_{j,\sigma} = \frac{1}{2}\int_{-\infty}^{\infty} N_j(E,\epsilon) \times\left[1+\exp\left(\frac{E+In_{j,-\sigma}+\sigma\mu_B H-\mu}{kT}\right)\right]^{-1}dE \ , \tag{8}$$

μ_B being the Bohr magneton.

In Secs. III A and III B, we calculate from the free energy the susceptibility χ and the transition temperature $T_M(x)$, fitting these quantities independently to experiment with a small set of parameters with physically reasonable values. It will be seen that best fits of $T_M(x)$ are obtained using values which are not entirely consistent with those used to fit χ, although for $x > 0.6$ a reasonably consistent set can be found which fits both quantities.

A. Susceptibility Anomalies

We may write the susceptibility $\chi(x, T)$ as

$$\chi(x,T) = \chi_0(x) + \chi_d(x,T) \ . \tag{9}$$

The major contributions to $\chi_0(x)$ come from the spin and orbital susceptibility of the electrons in wide bands, the diamagnetic susceptibility of the core electrons, and the Van Vleck paramagnetic susceptibility of the core and band electrons. Since a detailed knowledge of the band structure is required for its computation, any temperature dependence of the band Van Vleck paramagnetism is neglected, although such a term might be significant in La alloys.[17] For the sake of simplicity we assume that the observed T dependence arises solely from the contribution of the high-density e_g states χ_d. In computing χ_d, we assume that the Landau diamagnetism of the d electrons may be neglected in comparison with the Pauli spin paramagnetism, since the d electrons have a large effective mass.

We treat the d electrons in the Hartree-Fock approximation, obtaining an explicit expression for χ_d by direct differentiation of Eq. (7),

$$\chi_d = -\left(\frac{\partial^2 F_d}{\partial H^2}\right)_{H=0} = \mu_B^2 \sum_{j=1}^{2} N_j^{\text{eff}} \Big/ (1 - \tfrac{1}{4} I N_j^{\text{eff}}) \ , \tag{10}$$

where the temperature-dependent effective density of states N_j^{eff} is given as

$$N_j^{\text{eff}} = N_j f_j(E_j^l) \ . \tag{11}$$

Here the N_j are given by Eqs. (4) and (5) and $f_j(E)$ is

$$f_j(E) = \left[1+\exp\left(\frac{E+\frac{1}{2}In_j-\mu}{kT}\right)\right]^{-1} , \tag{12}$$

where E_j^l refers to the energy of the lower edge of the jth subband, and n_j is the total density of electrons in the jth subband.

Equations (10)–(12) give the enhanced susceptibility for two subbands in the Hartree-Fock approximation. In obtaining these expressions we have assumed that the number of electrons in the d band is small. Equation (10) may be written explicitly for the two structural phases in our model as

$$\chi_d^{\text{cubic}} = \mu_B^2 N_0 f(0)/[1 - \tfrac{1}{4} I N_0 f(0)] \tag{13}$$

and

$$\chi_d^{\text{tetra}} = \frac{\mu_B^2 N_0}{2}\left(\frac{f(U'\epsilon)}{1-\frac{1}{4}IN_0 f(U'\epsilon)} + \frac{f(-U'\epsilon)}{1-\frac{1}{4}IN_0 f(-U'\epsilon)}\right) . \tag{14}$$

Here $U'\epsilon$ is a Hartree-Fock renormalized deformation potential defined by

$$U'\epsilon = U\epsilon - \tfrac{1}{4}I(n_1 - n_2) , \tag{15}$$

and is assumed to be small compared to E_0. In Eq. (15) we see that the second term is strain dependent, making the renormalization approximately zero for small strains ($n_1 \cong n_2$), and a maximum of $\frac{1}{4}IQ_d$ when the strain is large enough so that the narrowed subband is almost entirely depopulated ($n_1 \cong Q_d$, $n_2 \cong 0$).

The Fermi function appearing in Eqs. (13) and (14) is given by

$$f(E) = (1 + e^{(E-\mu')/kT})^{-1} , \tag{16}$$

where

$$\mu' = \mu - \tfrac{1}{4}IQ_d .$$

As usual, conservation of the total number of electrons (in this case e_g plus wide-band s-d electrons) determines μ' and hence $f(E)$. In the cubic phase the conservation equation can be manipulated into the form

$$f^{\alpha/(\alpha+1)} = (1-f)e^{(E_F'/kT)} \tag{17}$$

if $E_F' > 0$ and

$$(1-f)^{(\alpha+1)/\alpha} = fe^{-E_F'/kT} \tag{18}$$

if $E_F' < 0$ and can be solved numerically for arbitrary α.

The quantity E_F' is the Hartree-Fock renormalized Fermi energy [defined as the cubic phase limit $\mu'(T \to 0) \equiv E_F'$]

$$E_F' = E_F/(1 + \tfrac{1}{4}IN_0) , \tag{19}$$

and $f \equiv f(0)$ is the Fermi function evaluated at the lower e_g band edge. In the tetragonal phase the equation for particle conservation is difficult to solve for arbitrary α. However, if α can be assumed small (which, in fact, we shall do), the conservation equation takes the form

$$e^{\mu'/kT} = [\cosh^2(U'\epsilon/kT) + e^{(2E_F'/kT)} - 1]^{1/2} - \cosh(U'\epsilon/kT) . \tag{20}$$

Figures 1(a)–1(f) show the variation of $\chi(x, T)$ with respect to its value at $T = 250$ K for a number of indium concentrations. When 10% of Ag has been replaced by In [Fig. 1(b)], the susceptibility changes radically, showing a rapid increase with decreasing temperature, with a large drop appearing at T_M. We attribute this anomalous behavior to the entering of the Fermi energy into the narrow e_g band of La, which is assumed to be empty for pure LaAg.

The experimental susceptibility of $LaAg_xIn_{1-x}$ for a silver concentration between 0.6 and 0.9 can easily be fitted in the cubic phase with Eqs. (13) and (17), the observed temperature dependence requiring the Fermi energy E_F' to be given by the numbers listed in Table I.

TABLE I. Parameter values used in the theoretical fits of $\chi(x, T)$ of $LaAg_xIn_{1-x}$. The quantities E_F' and $U'\epsilon$ are the Fermi energy and the deformation energy, respectively.

x	E_F' (K)	$U'\epsilon$ (K)
0.9	250	420
0.85	300	420
0.8	350	420
0.75	440	420
≤ 0.6	>1000	>3000

In the tetragonal phase the susceptibility is then fitted with Eqs. (14) and (20) using the deformation energy $U'\epsilon$ as given in Table I. Compatible with the parameters given in Table I is a concentration-independent set of values for N_0, I, and α: $N_0 = 1.55$ states/eV atom, $I = 0.548$ eV, and $\alpha = 0.25$. The theoretical fits are included as solid lines in Figs. 1(b)–1(f), which demonstrate good agreement between our simple Hartree-Fock theory and experiment.

Table I indicates that our model breaks down for $x \leq 0.6$, at least in a detailed description of the susceptibility, signifying that a radical departure from our density of states picture occurs at this point. For this reason the data shown in Fig. 2 have not been fitted.

Figure 3 shows the absolute magnitude of the susceptibility χ at 250 K versus silver concentration x. Over the concentration range $0.6 \leq x \leq 0.9$, where our model seems to have validity, one can deduce the contribution $\chi_0(x)$ to the susceptibility defined by Eq. (9); it is given in Table II.

B. Crystallographic Transformation Temperature

In order to determine the tetragonal instability, we consider the crystal to be in zero applied magnetic field. Then Eq. (7) becomes

$$F_d = \mu Q_d - kT\sum_{j=1}^{2}\int_{-\infty}^{\infty} N_j(E, \epsilon) \times \ln\left[1 + \exp\left(-\frac{E + \frac{1}{2}In_j - \mu}{kT}\right)\right] dE - \frac{1}{4}\sum_{j=1}^{2} In_j^2 . \tag{21}$$

Here n_j is the electron density in the jth subband, and $N_j(E, \epsilon)$ is given by Eqs. (4) and (5). The elastic modulus $(C_{11} - C_{12})$ is obtained by

$$C_{11} - C_{12} = \left(\frac{\partial^2 F}{\partial \epsilon^2}\right)_{\epsilon=0} \tag{22}$$

TABLE II. Values of the temperature-independent susceptibility $\chi_0(x)$ of $LaAg_xIn_{1-x}$ deduced from the experimental susceptibility at $T=250$ K.

x	0.9	0.85	0.80	0.75
$\chi_0(x)$ (10^{-5} emu/mole)	8.12	7.12	6.09	4.91

in the cubic state. Since the stable value of ϵ is that which minimizes F, the condition $(C_{11}-C_{12}) \leq 0$ indicates an instability of the cubic phase. By means of Eqs. (6), (21), and (22) one obtains for the elastic modulus

$$C_{11}-C_{12}=(a_{11}-a_{12})-U^2N_0A(T)\ . \tag{23}$$

Here $A(T)$ is given by

$$A(T)=f-\frac{IN_0(E_F'/E_0-\frac{1}{2}f)}{1+\frac{1}{4}IN_0f}+\frac{4kT}{E_0}\ln(1-f)$$
$$+4\left(\frac{kT}{E_0}\right)^2[2L_2(f)+\ln^2(1-f)]\ , \tag{24}$$

where E_F' is the Hartree-Fock renormalized Fermi energy given by Eq. (19), L_2 is the dilogarithm function defined by[18]

$$L_2(x)=-\int_0^x\frac{\ln(1-y)}{y}\,dy\ , \tag{25}$$

and $f=f(0)$ is the Fermi function, Eq. (16), evaluated at the lower e_g band edge.

The quantity $(a_{11}-a_{12})$ in Eq. (23) is defined by

$$a_{11}-a_{12}=\left(\frac{\partial^2F_0}{\partial\epsilon^2}\right)_{\epsilon=0}\ . \tag{26}$$

It is the contribution to the elastic modulus from all sources contained in F_0 and is in general positive and weakly temperature dependent. We ignore this temperature dependence. The second term on the right-hand side of Eq. (23) gives the part of $(C_{11}-C_{12})$ due to the e_g states. It is a negative contribution which "softens" the elastic modulus, and so is totally responsible for the tetragonal instability. The temperature T_M where the instability occurs is obtained from the condition

$$(a_{11}-a_{12})/U^2N_0=A(T_M)\ . \tag{27}$$

In deriving Eqs. (23) and (24) we have assumed that only a rather small number of electrons is in the e_g band at $T=0$. One arrives at a completely symmetric result for small hole concentrations (almost filled e_g states). As in the theory of Labbé and Friedel,[5-7] no tetragonal instability is possible for large electron (or hole) concentrations. This is in contrast to the theory of Rehwald *et al.*[9] It is contained in our theory and can be most easily seen by observing that the quantity $A(T)$ is a monotonically decreasing function of temperature, attaining its maximum value in the limit $T\to 0$:

$$A(T=0)=\frac{(2E_F'/E_0-1)^2}{1+\frac{1}{4}IN_0}\ . \tag{28}$$

From Eqs. (27) and (28) one first sees that a tetragonal instability is possible only if

$$U^2N_0>(a_{11}-a_{12})(1+\tfrac{1}{4}IN_0)\ . \tag{29}$$

Hence the instability is initiated when the product of the deformation potential with the density of states is large. Secondly, if Eq. (29) is satisfied, the maximum Fermi energy E_F^c for which the instability can occur is given by

$$E_F^c=\tfrac{1}{2}E_0\{1-[\gamma(1+\tfrac{1}{4}IN_0)]^{1/2}\}\ , \tag{30}$$

where

$$\gamma=(a_{11}-a_{12})/U^2N_0\ . \tag{31}$$

The cubic phase is always stable for $E_F'\leq 0$ and for $E_F^c\leq E_F'\leq\frac{1}{2}E_0$. (Corresponding results obtain for holes in a more than half-filled band.)

At first we attempt to fit $T_M(x)$ over the widest concentration range possible, irrespective of the parameter values assumed in the susceptibility fits of Sec. IV A. One may calculate T_M from Eqs. (24), (27), and (17), once a relation between the Fermi energy E_F' and the In concentration is assumed. We use the simple form

$$E_F'=(0.95-x)b\ , \tag{32}$$

where b is a constant. This form satisfies the requirement that $E_F'=0$ for $x=0.95$. [From experiment $T_M=0$ at this concentration, and from Eqs. (27), (28), and (29) we see that this requires $E_F'=0$.]

There is a simple relation between E_F^c defined by Eq. (30) and that Fermi energy E_F^m where the maximum T_M occurs, namely,

$$E_F^c/E_F^m=\tfrac{5}{2}[1/(1+\sqrt{\gamma})]\ . \tag{33}$$

Experimentally, the maximum T_M of about 192 K (cf. Fig. 4) occurs for $x_m=0.45$; and since the critical concentration corresponding to E_F^c can reasonably be chosen as $x_c=0.24$, one obtains from Eqs. (32) and (33) $\gamma=0.578$. After a choice is made for the s-d conduction-band density-of-states parameter α, the remaining parameters E_0, b, and IN_0 can be deduced from the experimental slope of T_M vs x at $x=0.95$ and the maximum T_M of $T_M=192$ K.

The two solid curves of Fig. 4, labeled A and B, are fits of the data using the correspondingly labeled sets of parameter values listed in Table III. These curves are representative of those given by the other unlabeled sets of values in Table III. From Table III one sees immediately that the only sensitive parameter is the Fermi en-

TABLE III. Parameter values used in the theoretical fits of the crystallographic transformation temperature T_M of $LaAg_xIn_{1-x}$. First column is the experimental slope of T_M vs x at $x=0.95$. The quantities α, IN_0, E_0, and b are, respectively, the contribution to the density of states due to the s-d conduction electrons, the intra-atomic Coulomb interaction times density of e_g states, bandwidth of e_g states, and Fermi energy divided by $(0.95-x)$.

$-\left(\frac{dT_M}{dx}\right)_{x=0.95}$ (K)	α	IN_0	E_0 (K)	b (K)	Fit shown in Fig. 4
860	0.0	0.45	5953.2	829.2	B
	0.1	0.7	6897.7	852.8	•••
	0.2	0.85	7574.8	866.9	•••
	0.3	1.0	8465.7	892.3	•••
1000	0.0	no fit	•••	•••	•••
	0.25	0.2	5160.9	802.0	A
	0.75	0.75	7142.4	861.1	•••
	1.5	1.0	8473.4	893.1	•••
860	0.25	0.85	79580.0	2550.0	C

ergy, the quantity b varying less than 100 K for all fits with the quality represented by curves A and B of Fig. 4.

It should be emphasized here that fits A and B of Fig. 4 are made using parameter values which are not consistent with those used to fit χ. The model is successful in fitting $T_M(x)$ over a much wider x range than χ, and in order to see if this result is only fortuitous, it is worthwhile to attempt a fit of $T_M(x)$ using parameter values that are as consistent as possible with the susceptibility fits. This is shown as the dashed curve C in Fig. 4, using $\gamma=0.79$ and the values labeled C in Table III. The parameters used for curve C are completely consistent with those of the χ fits except for $E_F'(x)$, for which no completely consistent values can be found. Comparison of $E_F'(x)$, needed to fit χ and T_M, is made in Fig. 7. Best fits of $T_M(x)$ (curves A and B of Fig. 4) are made with the solid straight line; whereas the fit most consistent with the χ fits (curve C of Fig. 4) is made with the dashed straight line. The solid curved line in Fig. 7 is that used to fit $\chi(x, T)$. The χ fits are found to be very sensitive to the value of E_F'. An example of this sensitivity is shown in Fig. (1b), where the dashed curve represents a fit using $E_F'=200$ K and the solid curve represents a fit using $E_F'=250$ K. It should be emphasized that each of these fits was made independently, using the best possible values of the other parameters.

IV. DISCUSSION

We have shown that the behavior of the measured susceptibility $\chi(x, T)$ of $LaAg_xIn_{1-x}$ can be explained for $0.6 \leq x \leq 0.9$ using a simple density-of-states model and giving a small set of parameters physically reasonable values, under the assumption that the observed structural instability arises from a bandlike Jahn-Teller effect and that the increase in In concentration causes a general increase in the Fermi energy E_F' into a fixed density-of-states peak. The description is not con-

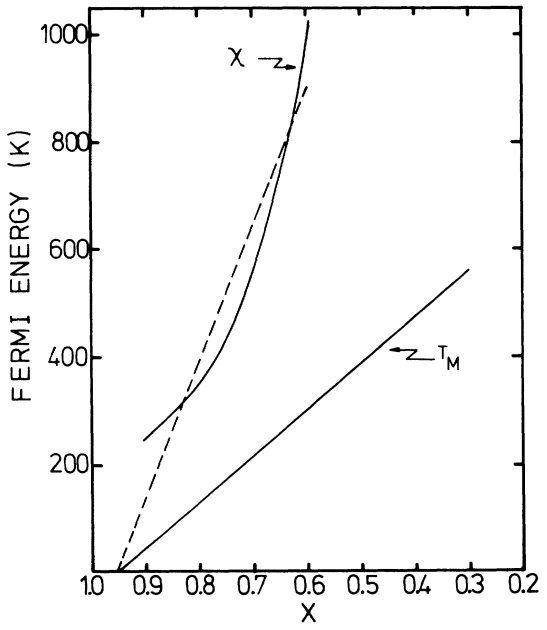

FIG. 7. Fermi energy E_F' vs x in $LaAg_xIn_{1-x}$. The solid straight line is used to fit the transition temperature $T_M(x)$ in the range $0.25 \leq x \leq 1.0$. The dashed straight line is used to fit $T_M(x)$ in the range $0.6 \leq x \leq 1.0$, whereas the solid curved line is used to fit the susceptibility $\chi(x, T)$ in the range $0.6 \leq x \leq 1.0$.

sistent, however, since the value of the Fermi energy needed to fit the temperature dependence of χ is always larger than that needed to predict correctly the crystalline-phase transition temperature $T_M(x)$. (A similar discrepancy was found by Rehwald *et al.*[9] in Nb_3Sn.) In fact, a good description of $T_M(x)$ is obtained over the much larger concentration region $0.25 \leq x \leq 1.0$ within the same model, but using values of E_F' completely inconsistent with the fits of χ. Using the most consistent values of $E_F'(x)$ possible, a good description of $T_M(x)$ is obtained for $0.6 < x \leq 1.0$, and the theoretical fits of χ and $T_M(x)$ break down at approximately the same value of x. It should be noted that this most consistent fit of $T_M(x)$ uses a value ~ 7 eV for the d band width as compared to a value ~ 0.7 eV used for the wider x-range fits of $T_M(x)$. The larger value of E_0 might be in more reasonable agreement with d bandwidths in transition elements, but one expects narrower bands in alloys since the transition metal ions are more widely separated in this case. The width of the density-of-states peak due to the La-e_g electrons should be even smaller than this.

The breakdown of our theoretical description at the larger In concentrations is probably due to substantial departures from our density-of-states model. The supposition that radical changes in the electronic structure do occur in the In-rich solid solutions is supported by the fact that compounds with $x \leq 0.1$ cannot be prepared in a one-to-one stoichiometry. The value $N_0 = 1.55$ states/eV atom deduced from the fits to χ is reasonable for a narrow d band, being much larger than that of an ordinary wide s band. The same value $IN_0 = 0.85$ may be used in good fits of both T_M and χ. Since IN_0 enters the enhanced susceptibility formulas, Eqs. (13) and (14), with a factor $\leq \frac{1}{4}$, this value is felt to be not unreasonable.

In order to fit the difference in χ at T_M for the two phases, we must use $U'\epsilon = 420$ K for all x values in the range $0.6 < x \leq 0.9$. In this concentration range both ϵ and the cubic-phase lattice parameter increase (Fig. 5). This implies that the deformation potential U' decreases since for larger ionic separations the overlap of the d-band orbitals changes less with applied strain. The fact that a constant $\gamma = (a_{11} - a_{12})/U^2 N_0$ was needed in fitting $T_M(x)$ could imply that $(a_{11} - a_{12})$ becomes softer as In is added.

Direct calculation of $U'\epsilon$ from minimizing the free energy gives a value which, in contrast to the values given in Table I, increases somewhat with increasing In concentrations, but is of the same order as $U'\epsilon$ deduced from the χ fits. It should be pointed out that our model cannot predict whether a structure with a c/a ratio smaller or larger than 1 is stable since the free energy is symmetric, $F(\epsilon) = F(-\epsilon)$. Whereas our theory clearly describes a second-order phase transition, it is not clear from the experimental material at hand whether the crystal transformation observed in $LaAg_xIn_{1-x}$ (and similarly in LaCd, $CeAg_xIn_{1-x}$) is of first or second order.

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