MAGNETIC PROPERTIES OF INDIUM ALLOYS. I. SOLID SOLUTIONS OF Cd, Sn, AND Pb IN In

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The effect of temperature ($20.4^{\circ} K \le T < 300^{\circ} K$) and electron density (mean valence 2.95 < Z < 3.10) on the magnetic susceptibility of indium is studied. The anomalous diamagnetism of indium disappears when Z is increased by 2%. Difficulties in interpreting χ (T, Z) on the basis of the Landau-Peierls contribution apparently signify that inter-band interactions play an important role. Information on the electron structure of indium alloys is obtained on the basis of the contribution of inter-band interactions.

HE classification of magnetic substances according to the character of the temperature variation of their magnetic susceptibilities $\chi^{[1]}$ has disclosed a group of elements with the same kind of unusual temperature dependence of the magnetism of the conduction electrons.^[2] The manifestation of a dependence $\chi(T)$ for electrons is evidence that the characteristic energies of the states responsible for the magnetism are small. These states correspond to small sections of the Fermi surface, which give long-period quantum oscillations in x at low temperatures (de Haasvan Alphen effect). According to current notions such states arise in multivalent metals close to the faces of the Brillouin zone^[3], and are determined by the energy gaps at the faces. Since in metals the gaps are inaccessible to direct investigations, the study of the parameters of these states gives important information about the effective lattice potential. [3,4]

Almost all existing methods for studying the fine details of an electronic spectrum require that the objects of investigation have a high degree of purity satisfying the condition $\omega \tau \sim 1$, where ω is the Larmor precession frequency of the electron and τ is the time between collisions. Collisions are not important for the monotonic part of the function χ (T), which can therefore be used to investigate the states near the Fermi level of a pure metal by changing the electron population with impurities of different valence.

The states of interest to us are usually represented by a small group of charges (electrons or holes) with a low end-point energy, approximately ellipsoidal Fermi surface, and small and anisotropic effective masses.^[5] Because of the insignificant charge density, the spin paramagnetism of such a group is usually not taken into account, and the dominating contribution due to the small effective masses is considered to be the Landau-Peierls diamagnetic susceptibility χ_{LP} .^[6]

For a group described by an ellipsoid of revolution $(m_1 = m_2 \neq m_3)$, this part of the susceptibility has at T = 0 the form

$$\chi_{\perp}^{0} \equiv \chi_{1} = \chi_{2} = -0.097 \left(E_{0} m_{0} / m_{3} \right)^{\frac{1}{2}},$$

$$\chi_{\parallel}^{0} \equiv \chi_{3} = \chi_{\perp}^{0} m_{3} / m_{1},$$
 (1)

where χ^0 is the volume susceptibility, E_0 is the end-point energy of the group, and the subscripts 1, 2, 3 indicate direction relative to the principal axes. The temperature dependence of χ_{LP} was obtained in ^[7,8] with the following asymptotes:

$$T \ll T_0$$
: $\chi(T) = \chi^0 [1 - \frac{1}{12} \pi^2 (T / T_0)^2],$ (2)

$$T \gg T_0$$
: $\chi(T) = \frac{2}{3}\chi^0 T_0 / T$, (3)

where $T_0 = E_0/k$ is the limiting temperature (degeneracy temperature), and χ^0 is determined from (1). The behavior of $\chi_{LP}(T)$ for a large number of coexisting groups depends on the relation of their end-point energies.^[8] Thus, the dependence of the susceptibility on temperature and electron population (the average valence of the atoms Z) permits one to obtain rather complete information about the small groups: E_0 , m_i and their variation with population, sign of the charges, and ratio of the energies of the groups, if there are several of them.

There are more general formulas for the orbital magnetism^[9] that include, besides the quantity χ_{LP} , contributions from the non-square law of the spectrum of the inter-band transitions, etc.

The form of these, however, permits neither numerical application nor a clear physical interpretation. Nevertheless, a modern analysis^[10] of the experimental behavior of χ (T, Z) in alloys of Bi^[11] indicates that the contribution of the interband interactions is significant. We note that the cited reference is the only adequately complete investigation in this area.

The purpose of the present paper is the clarification of the real possibilities of an investigation of the dependence χ (T, Z) as a method of studying the fine details of the electronic spectrum. It includes: a) a determination of the adequacy of the Landau-Peierls approximation for describing χ (T, Z) in the case of alloys of a normal multivalent metal (in contradistinction to the semimetal Bi), and b) the extraction, on the basis of this approximation, of the maximum information about the spectrum and its variation under the influence of impurities. The final goal of such investigations is information about the electronlattice interaction.

As an object for investigation we chose indium, which has the characteristic χ (T) dependence [see Eqs. (2) and (3)] in a convenient temperature region^[2] and wide limits of existence of solid solutions with its closest neighbors in the periodic table.^[12]

1. SAMPLES, METHOD OF INVESTIGATION, AND APPARATUS

Monocrystalline samples of solid solutions of the systems In-Cd (0 to 5 atomic % Cd), In-Sn (0 to 4 at. % Sn), In-Pb (0 to 10 at. % Pb) were prepared by the following method. Weighed portions of the pure components were melted and carefully mixed in a quartz test tube in a vacuum of ~ 10^{-3} Torr (the alloys with Cd in a hydrogen atmosphere). The impurity content of the starting metals was not greater than 10^{-4} %. The alloys with impurity content less than one percent were obtained by successive dilution. The correspondence of the final and initial compositions containing volatile admixtures was monitored by the weight loss of the alloys, since there was not enough material to make a quantitative analysis of the samples. Significant errors, indicated in the graphs, were obtained only for highly volatile Cd.

Monocrystals of almost spherical shape weighing about 60 mg were grown in graphite molds in vacuum or inert atmosphere by slow cooling of the oven. Although the small segregation coefficient in In alloys guarantees their uniformity when they solidify, [12,13] the majority of the samples underwent almost a year's diffusion annealing. The experiment showed, however, that there was no necessity in this; to obtain the equilibrium lattice parameters it turned out to be more effective to keep the samples at room temperature for a few days after preparation.^[14] The monocrystals were oriented in an optical goniometer using suitably etched reflecting spots.

The magnetic susceptibility was measured by the Faraday method with an autocompensated balance^[15] in fields of up to 8000 G at the sample location. The magnitude of χ_{\perp} for highly purified zinc, measured previously by an absolute method, ^[16] served as a standard. For the temperature investigations, the natural warming rate of the apparatus ~ 2 deg/min from 20.4° K to room temperature was utilized. The temperature was measured with a copper-constantan thermocouple in thermal equilibrium with the sample at the indicated warming rate.

The susceptibility along the two principal directions was recorded with an ÉPP-09 potentiometer, in the form of a series of closely spaced points, replaced by continuous curves on the graphs presented here.

Some of the samples showed the weak field dependence χ (H) characteristic of ferromagnetic traces; these were apparently introduced in the course of preparation and mounting. The effect of the ferromagnetism was eliminated by extrapolating χ (H⁻¹) to H = $\infty^{[17]}$; the difference between the susceptibility at maximum field and the extrapolated susceptibility amounted to 0–5%. The extrapolated values of χ are presented here.

The accuracy of the measurements was: temperature, $\pm 1.5^{\circ}$; relative changes of χ with temperature, $\pm 1\%$; absolute values of χ , $\pm 1.5\%$ with respect to calibration and $\pm 3\%$ taking into account the possible systematic error in the calibration. These figures were estimated for the values of χ for pure In at room temperature; naturally, they will be somewhat worse for the smallest values of χ .

2. RESULTS OF THE INVESTIGATION

The present communication includes results of the investigation of 20.4° K \leq T $< 300^{\circ}$ K of the principal values of the susceptibility of alloys of In with its periodic-table neighbors that differ by a unit of valence. Introduction of Cd lowers, and of Sn and Pb raises the Z of the alloys. The behavior of χ was studied in the α -phase with face-centered tetragonal lattice (c/a > 1). The behavior of the constant-valence alloys In—Tl and In—Ga with Z = 3 and the β -phase of In—Sn alloys will be the subject of later papers. The dependences of the susceptibility along the axes c (χ_{\parallel}) and a (χ_{\perp}) on the impurity concentration at T = 20.4°K and T = 293°K are given in Figs. 1 and 2, and the corresponding temperature dependences in Figs. 3 and 4. For convenience, the impurity concentration scale has been converted into a scale of mean valence Z, with the assumption that the valences of the pure components correspond to their position in the periodic table.

We note the following peculiarities of the behavior of χ (20°K, Z) $\approx \chi$ (0°K, Z) with increasing Z:

1. χ_{\parallel} increases, attains a maximum at Z = 2.98, and rapidly falls with a sag toward the concentration axis, tending toward saturation.



FIG. 1. Plots of $\chi_{\parallel} \chi_{\perp}$ against Z for indium alloys at $T = 20.4^{\circ}$ K. The filled and open circles pertain to measurements in different electromagnets.



FIG. 2. Dependence of χ_{\parallel} and χ_{\perp} on Z for alloys of indium at T = 293°K. (χ^{b} - background susceptibility).





FIG. 3. Temperature dependence of χ_{\parallel} for the alloys: a - In-Cd, b - In-Sn, c - In-Pb.

2. χ_{\perp} falls monotonically; for Z > 2.98, its behavior is similar to χ_{\parallel} .

3. The anisotropy of the susceptibility $\Delta \chi = \chi_{||} - \chi_{\perp}$ repeats the behavior of $\chi_{||}$, then changes sign for Z > 3.05, grows somewhat, and tends to saturation.

4. The effect of Sn and Pb is the same, if it is assumed that the effective valence of the Pb atoms in the alloy is 1.2 times lower than Sn. Keeping in mind that the reason for the differences is not necessarily the valence, we decided not to change the scale of Z for the In—Pb system.

The behavior of χ (293° K, Z) repeats the behavior of χ (20° K, Z), but the magnitudes of the susceptibility and their changes are markedly less.



FIG. 4. Temperature dependence of χ_{\perp} for the alloys: a - In-Cd, b - In-Sn, c - In-Pb.

The temperature dependence χ (T) is characterized by the following:

1. Up to Z \sim 2.98, χ (T) along both directions agrees with Eqs. (2) and (3).

2. For Z > 2.98 the temperature dependence weakens and is distorted: $\chi_{||}$ shows a maximum slightly shifted towards high temperatures.

3. χ_{\perp} at Z \sim 3.01 and $\chi_{||}$ at Z \sim 3.05 are independent of temperature.

4. With further increase in Z, χ repeats the foregoing behavior, but with a different sign of d χ /dT and sharper curvature.

5. χ_{\parallel} displays a greater temperature dependence than χ_{\perp} for almost all Z.

As can be seen, the contribution to the susceptibility with the sharpest dependence on temperature appears along the four-fold axis in the range of electron concentrations 2.95 < Z < 3.05. It is to just this contribution to χ that we shall pay principal attention in the discussion.

3. DISCUSSION OF THE RESULTS

We shall try to describe the observed susceptibility and its temperature dependence by means of a Landau-Peierls contribution in the simplest case of a single group of charges. For Z < 3 the character of the χ (T) curves is close to that predicted by Eqs. (2) and (3). Combining the accurate theoretical χ (T) dependence (e.g., from [8]) with the experimental one, we obtain the values of χ^0 and T₀. Instead of χ^0 we give in Fig. 2 the background susceptibility for the small group $\chi_i^b = \chi_i(0^\circ, Z) - \chi_i^0(Z)$. For pure indium χ^b turns out to be close to the total magnitude of χ of a gas of free electrons and ions (indicated in Fig. 2 by a cross). The weak temperature dependence of χ^b may serve as the source of the discrepancies between the experimental and theoretical curves in the intermediate temperature region (Fig. 3a). The small inaccuracy in the parameters associated with these does not affect the conclusions that follow.

Despite the fact that a change of 1.5% in the electron concentration alters the level of the chemical potential of the free-electron gas of indium by an amount $\Delta T \sim 1000^{\circ}$ K, T₀ for the small group is changed very little (Fig. 5). The states responsible for the magnetism are found to be the energetically "stabilized" ones for 2.96 < Z < 3. The latter is also confirmed by the behavior of the ratio $\chi'(20^\circ)/\chi'(293^\circ)$ (see table). Differentiation of the relation (3) with respect to Z gives for this ratio an expression agreeing with experiment for $T_0 \sim 140^{\circ}$ K and $T'_0 \approx 0$ even in the region Z > 3, where the distortion of the temperature dependence of χ precludes comparison with theory. Such "stabilization" of the electronic structure in indium is characteristic, as shown in



FIG. 5. Dependence of T_0 on Z for In alloys.

z	$-x_{\parallel}$ (20,4°K), 10^{-7} cm ³ /g	$\frac{x'(2^{\circ\prime})/x'(293^{\circ})}{x' = dx/dZ}$		m _i /m _• ·104	
$2.96 \\ 3,00 \\ 3.05$	4,84 4,55 0,48	$3.5 \\ 3.2$	 3,0 3.5	0,86 2,8 	4,6 42 —

^[18], of states in the farthest corners of the Brillouin zone (denoted below by W'). This exhausts the seeming agreement of experiment with the theory of the Landau-Peierls contribution.

An analysis of the model of almost-free electrons shows that a possible small group of charges at the points W' consist of two "ellipsoids." Replacing these in the calculation by one decreases the value of the effective masses by $(2)^{1/2}$ without changing the subsequent conclusions. Serious discrepancies between experiment and theory consist in the following.

1. The effective masses obtained from Eq. (1) are improbably small (see table).

2. In the fields used the relation $\mu^* H > kT_0$ is fulfilled, where μ^* is the effective Bohr magneton. In this case Eqs. (1)—(3) lose their validity, and the susceptibility of a free-electron gas should display at T = 0 a strong dependence on the magnitude of the magnetic field^[19]:

$$\chi_H / \chi_0 = \frac{8}{27} (kT_0 / \mu^* H)^4.$$
(4)

This dependence is determined by the diamagnetic part of χ and can apparently be applied to the case of the small group. The actual dependence of χ on H is weak (Sec. 1) and contradicts the initial inequality.

3. The principal cause of the changes in χ is the change in the effective masses of the charges, and not in the number of particles in the group (otherwise, in conflict with experiment, the quantity χ (Z) should vanish with infinite derivative, since $\chi \sim n^{1/3}$, where n is the number of particles per atom in the group). Then the reversal of sign in $d\chi/dT$ at Z ~ 3.05 presumes a completely improbable increase in the effective masses by four orders, to a value ~ m₀, in a narrow interval of change in Z. Besides this, the curvature of the c/a vs. Z^[18] curve is opposite to that of the m₃/m₁ vs. Z curve, which is naturally connected with the anisotropy of the lattice.

4. The comparison with theory of the dependence χ (T) for one group is justified for a preliminary estimate of the parameters. In indium, along with the possible small group, there exist large ones—holes (T₀ ~ 100 000° K) and electrons (T₀ > 2000° K).^[5,20] The marked difference in the end-point energies of the small and large groups permits full use of dependences χ (T) found in ^[8] for several groups, for when T \leq T₀ the behavior of the small group does not depend in this case on the sign of the charges, on the exact relation of the boundary energies, and, apparently, on the validity of the condition n_e = n_h used in the theory. As before, the susceptibility χ of a small group falls with increasing T, then increases after passing through a minimum at $T \sim T_0$. The temperature modulation of χ for indium alloys is approximately

$$\chi(0^{0}) - \chi(T_{0}) < 0.1 \chi^{0}, \qquad (5)$$

and the parameters of the group are different: $T_0 \sim 300^{\circ}$ K and χ^0 is seven times greater than the value determined earlier. The disagreement with experiment is made worse, since: a) in order to describe the increased value of χ^0 it is necessary to decrease the anomalous masses 30 times even without this; b) there is no mechanism capable of compensating such a magnitude of χ^0 down to the actual observed value of χ (20°); a calculation of the theoretical value of χ^b for pure indium on the basis of electronic heat capacity^[21] changes the value marked in Fig. 2 little; c) the ratio $\chi'(20^{\circ})/\chi'(293^{\circ}) \approx 1$ that results from condition (5) is not obtained (see the table).

5. The detailed character of the temperature dependence of χ when $Z \gtrsim 3$ cannot be explained by either the simplest or the more complex theory.

In summarizing the comparison of the susceptibility of indium alloys with the Landau-Peierls theory, it can be asserted that this does not describe either the absolute magnitude of the diamagnetism or the peculiarities of its behavior with change of temperature and electron concentration. The result, as is seen from item 4 above, does not depend on any arbitrariness in the choice of the number of ellipsoids describing the small group.

All the information available at present on the electronic structure of In pertains to large groups. ^[5,20] An extremely sensitive method, the de Haas -van Alphen effect, does not detect any anomalous small groups or narrow necks capable of giving the observed contribution to χ . Our special search for oscillations in weak fields due to small groups with the calculated parameters gave a negative result (in a field of ~ 500 G, the expected period is ~ 500 G). According to the free-electron model, out of the four zones abutting the corner point W' (Fig. 6), small groups can arise only in the first (holes) and fourth (electrons). Application of the model to the interpretation of the dependence of c/a on Z in In alloys shows^[18] that the states of these four zones are separated in W' by small energy gaps ($\Delta E < 0.1 \text{ eV}$) and down to Z = 2.98are filled only in the first zone. Then the second and third are filled, and probably only when $Z \sim 3.06$ is the fourth zone filled. Therefore, the anomalous diamagnetism appears in that region of Z where there are no small groups, and is not associated with the Landau-Peierls contribution.



W

W

FIG. 6. Section of the Fermi surface of indium by a (100) face in a corner of the Brillouin zone on the model of almost-free electrons (similar $to^{[4]}$). The elongation of a possible hole group is seen in zone I; the possible electron states in zone IV have the same aspect.

The source of the strong diamagnetism in the situation considered can be virtual transitions of the electrons between zones that lie close together, the contribution of which for small masses has been neglected until recently. Adams^[22] has pointed out the importance of this mechanism expressly for small masses (small energy gaps) and obtained a formula for its estimation:

$$\chi_{\rm A} = (m_0 / m^*) \chi_{\rm L}^0, \tag{6}$$

where $\chi_{\rm A}$ is the Adams contribution, $\chi_{\rm L}^0$ is the Landau diamagnetism for a free-electron gas, and m* is the average value of the effective masses in the plane perpendicular to H. The exact equations containing the Adams contribution^[9] require presently unknown data about the electronic wave functions. The largest value of χ_A is observed in the case when the lowest of the zones separated by a small gap is completely filled, and the highest is empty. Both the freeing of states in the first zone and the filling of the second decrease the diamagnetism. Such behavior is confirmed by Bi alloys, the magnetism of which, as follows from a detailed comparison of the experimental value of χ with χ_{LP} , [10,23] is due to the Adams contribution. Unfortunately, there is no detailed theory for calculating χ_{A} .

The absolute magnitude of χ for In can be interpreted by means of the Adams contribution [Eq. (6)] for completely reasonable values of m* The character of the anisotropy of the susceptibility agrees with the anisotropy of the effective masses of the states at W'. We refrain from a quantitative comparison since the states responsible for the magnetism are apparently only those in the corners and not on the faces of the zone, as postulated in ^[22]. The atomic susceptibility χ_{at}^{0} of In turns out to be an order of magnitude smaller than χ^0_{at} for Bi, in approximate correspondence with the relation between the energy gaps ($\Delta E \sim 0.1 \text{ eV}$ for In; $\Delta E \sim 0.023 \text{ eV}$ in Bi^[24]).

The χ (Z) dependence for In alloys also agrees qualitatively with the Adams contribution from filled corners W' of the first zone and free states in the others. Down to Z = 2.98 only the anisotropy of the susceptibility changes in step with the change in the c/a ratio. Occupation of the upper states when Z > 2.98 leads to a decrease in χ_A and possibly to a disappearance of this contribution at $Z \sim 3.06$, when states in the fourth zone are filled. It should be noted that the forms of the $\chi(Z)$ dependence in In and Bi alloys are completely analogous; the sharp temperature dependences of χ of these systems, evidently a characteristic property of the contribution we are discussing, are also very similar. Qualitative conclusions based on an analysis of the χ_A contribution permit the elimination of many of the contradictions coming out of the Landau-Peierls equations and agree well with the data on the effect of the Fermi surface on lattice parameters.^[18]

As is seen, the manifestation of a contribution from interband interactions is not a privilege of such a unique semi-metal as Bi and can be encountered in rather general cases. The discrepancy between the parameters of the electronic states determined from the monotonic and oscillatory parts of χ can serve as an indication of the significance of χ_A . Note that the contribution of interband interactions is scarcely reflected in the quantum oscillations of the susceptibility.^[23] In particular, it can be assumed that the susceptibility of Cd also is due to the Adams contribution, since Cd, like In, shows a sharp and anisotropic dependence χ (T) with $T_0 \sim 100^\circ\, K,$ while the quantity T_0 determined from the de Haas-van Alphen effect amounts to 2000° K.^[2]

After the states responsible for interband interactions are filled, the χA contribution cannot appear in the α -phase and other modifications of indium alloys, and the Landau-Peierls susceptibility becomes noticeable. This question will be discussed later.

CONCLUSION

A short summary comes down to the following:

1) The temperature-dependent susceptibility of In alloys cannot be successfully described by a Landau-Peierls contribution.

2) It is more natural, albeit less customary, to describe this diamagnetism by a contribution

arising from virtual transitions between zones separated by a small energy gap (Adams contribution).

3) In the framework of qualitative notions about the Adams contribution, the observed susceptibility agrees well with the particulars of the electronic spectrum determined in [18], confirming them.

4) The Adams contribution can be expected to appear in rather frequent cases (e.g., in Cd).

5) Despite the absence of a theory, a knowledge of χ_A allows one to obtain information on the occupied zones and energy gaps in metals.

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