

TEMPERATURE DEPENDENCE OF THE MAGNETIC SUSCEPTIBILITY OF INDIUM,
LEAD, AND TIN CRYSTALS

B. N. ALEKSANDROV, B. I. VERKIN, and I. V. SVECHKAREV

Physico-Technical Institute, Academy of Sciences, Ukrainian S.S.R.

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A new version of the Faraday method is proposed for measuring the magnetic susceptibility of In, Pb, and Sn crystals in the range from room temperature to 20.4°K. The $\chi(T)$ curves thus obtained are characteristic of the whole group of elements which exhibit the long-period de Haas—van Alphen effect. This indicates the existence of small electron groups.

ATTEMPTS to classify magnetic substances by the sign of their experimentally-measured susceptibility have not been able to reveal sufficiently the connection between the magnetic properties and the nature of the solid state of the elements. The measured susceptibility is the sum of several terms

$$\chi_{\text{exp}} = \chi_{\text{ion}}^{\text{para}} + \chi_{\text{ion}}^{\text{dia}} + \chi_{\text{el}}^{\text{para}} + \chi_{\text{el}}^{\text{dia}} \quad (1)$$

and its sign does not unambiguously determine which of the terms plays the largest part.

A systematic study of the de Haas—van Alphen effect,¹ and an investigation of the experimental data on the temperature dependence of the susceptibility of elements have made it possible to propose a new classification of magnetic substances,² based on the nature of the temperature dependence of their susceptibility. Such a classification also allows to determine the term which is mainly responsible for the magnetic properties, which turn out to be closely related to the place the element occupies in the periodic table. Thus, elements which exhibit the de Haas—van Alphen effect in normal fields form a single group in the long periodic system. The investigation of highly purified elements of this group to date — Bi (reference 3), Sb (reference 4), Zn (reference 5), Cd (reference 6), graphite (reference 7), and Ga (reference 8) — discloses (contrary to existing opinion), a considerable increase of diamagnetism with decreasing temperature, at least in certain directions.

The temperature dependence of the susceptibility of these elements is probably connected with the presence of small groups of electrons, and should consequently be characteristic of all elements exhibiting a long-period de Haas—van Alphen effect.² In order to check this assumption, we have investigated the temperature dependence

of the magnetic susceptibility of three pure metals of cubic and tetragonal structure belonging to this group: Pb, I, and Sn.

PREPARATION OF THE SPECIMENS

Spherically shaped single crystals were grown in glass ampules by Bridgeman's method. The glass was removed by dipping in fluoric acid. The contaminated layer of the specimens was then removed with the aid of suitable pickling solutions, and the reflecting planes appeared. The orientation of the single crystal was determined with the aid of a two-dial Chapskiĭ goniometer.¹⁰ A small quartz sleeve was attached to the specimen with Zapon lacquer on the goniometer stage, to make the shoulder produced by the center of gravity of the crystal relative to the length of the sleeve coincide with the chosen crystallographic direction. This was the direction along which the susceptibility of the specimen was measured.

The purity of the investigated metals was characterized by the ratio $\delta = R_{4.2^\circ\text{K}}/R_{\text{room}}$, where $R_{4.2^\circ\text{K}}$ is the electric resistance at a temperature of 4.2°K, and R_{room} is the resistance at room temperature.

We prepared and investigated: a) one tin specimen of high purity, obtained in the laboratory by repeated zone recrystallization and prolonged heating in vacuum;¹¹ the value of δ of this specimen was 1.8×10^{-5} ; b) two lead specimens of the firm "Kalbaum" with $\delta = 5.4 \times 10^{-5}$; c) two indium specimens with $\delta = 1.2 \times 10^{-4}$. The mass of the specimens was 0.35 – 0.5 g.

EXPERIMENTAL METHOD AND APPARATUS

The principal values of the susceptibility were measured on a modified torsion balance by the

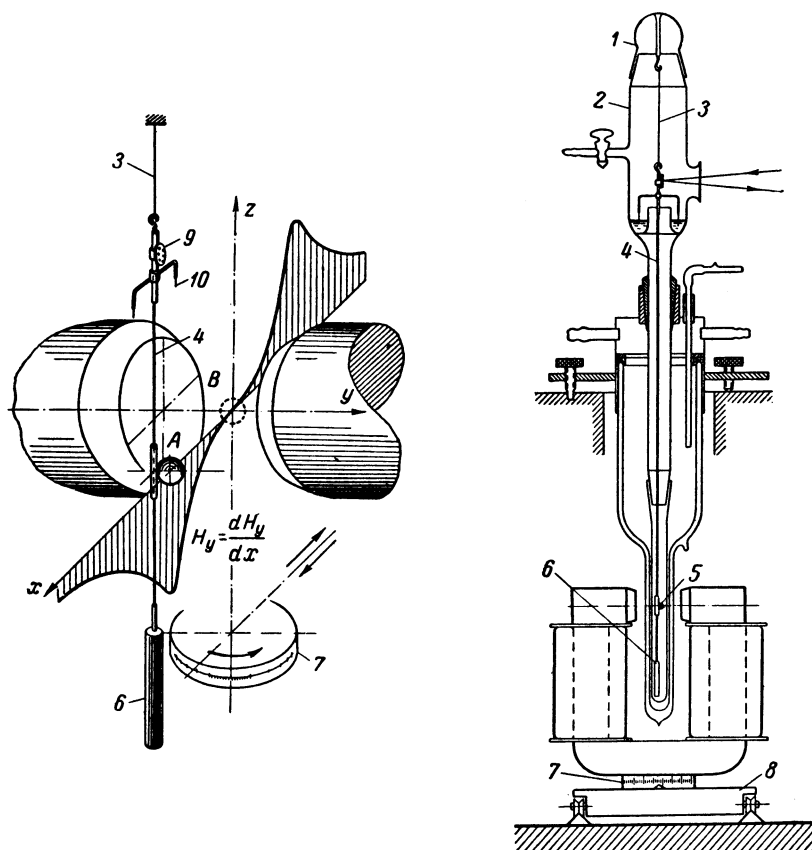


FIG. 1. Diagram of the apparatus and the position of the specimen in the magnetic field.

Faraday method (Fig. 1).

A system consisting of a small mirror 9, a damper 10, and a quartz rod 4, was suspended from the glass portion 2 of the apparatus by means of an elastic metal thread 3; a quartz sleeve with the specimen 5 was tightly fitted over the quartz rod. By displacing the electromagnet on the carriage 8, by a suitable pasting of the sleeve with the specimen, and by a rotation of the cap 1, the sample was placed level with the centers of the pole pieces and remained equidistant from them when the carriage with the magnet was displaced along the rails. The investigated crystallographic axis (and consequently also the "shoulder") were directed along the field. Thus, the specimen was only acted upon by the field gradient in the direction of the x axis. A cylindrical weight 6 fixed the quartz rod as the axis of rotation of the suspended system. The weight was prepared of extremely pure polycrystalline tin (so that it had a small susceptibility and anisotropy), and was placed in a very weak field; it practically introduced no distortion in the reading of the instrument. The force acting upon the specimen in an inhomogeneous field was applied to the shoulder 1 formed as a result of the eccentric position of the sample relative to the axis of rotation, and produced a

twisting torque balanced by the elasticity of the metallic thread. The angle of rotation of the suspended system was determined with the aid of a mirror and a scale. In equilibrium

$$k\varphi = m\chi l H_y dH_y/dx, \quad (2)$$

where φ is the angle of rotation of the mirror, and k is the elastic modulus of the thread. The measurements were conducted by a relative method at the point A of the field where $H_y dH_y/dx$ had a maximum value; point A was found by displacing the electromagnet along the rails until a maximum deviation for a given magnet current was obtained.

In this case

$$\chi = \chi_0(m_0 l_0 k / m l k_0)(\alpha/\alpha_0), \quad (3)$$

where the quantities with the zero subscript refer to the standard substance, and those without a subscript to the investigated substance; the ratio α/α_0 is taken with an equal current flowing through the magnet. Twice-distilled water in a spherical glass ampule, whose dimensions differed little from those of the investigated specimens, served as the standard substance. The calibration consisted of recording the dependence of the deflection of the pointer along the scale on the current flowing through the magnet at points in which

$H_y dH_y/dx$ was a maximum, and averaging it over the following four positions of the ampule: a) on both sides of the pole pieces; b) in the same positions after the sleeve with the ampule has been turned through 180° . Such averaging allows to exclude the weak anisotropy of the suspended system, and the change in the magnitude of the "shoulder" due to a possible small bend of the quartz rod and also due to the possibility that the rod and the centering weight 6 do not have a common axis. The ampule was dried by evacuating the instrument, and an analogous dependence was recorded for the empty ampule. The true deflections for water were found by subtracting the curves. The specific susceptibility of water was taken to be $0.720 \text{ cm}^3/\text{gauss}$.

The measurements of the absolute values of the susceptibility of the samples and its temperature dependence were conducted in the same way as the calibration. The effect of the medium was excluded by evacuating the instrument and filling it with hydrogen at a low pressure.

The method which was used allowed to determine, in a single experiment, both one of the principal values of the susceptibility and its anisotropy in the xy plane, by bringing the crystal into a region of homogeneous field (point B). When the crystal was mounted so that the above plane contained its principal crystallographic axis, then the angle of rotation of the suspended system due to the orienting action of the field was

$$\varphi = (mH^2 \sin 2\theta/2k) (\chi_{\parallel} - \chi_{\perp}), \quad (4)$$

where θ is the angle between the principal axis and the direction of the field (the magnet was free to rotate about the z axis, the angles of rotation were read on dial 7).

The mass of the crystal was determined by weighing, while the shoulder position relative to the axis of the sleeve was measured with a comparator; a correction was introduced for the commensurability of the mass of the crystal (0.5 g) and the fixing weight (4 g), because of which the axis of rotation did not coincide with the rod 4. Thin tungsten wires with diameters 0.05 and 0.03 mm and elastic moduli 6.44 and 0.844 dyne-cm/rad respectively were used as elastic threads.

In the course of the measurements we tried a quasi-elastic bifilar suspension; the idea is that during a rotation of a system suspended on two parallel threads there appears a weight component tending to return the system to its previous position. An elementary calculation shows that the elastic modulus of such a suspension (neglecting the elasticity of the threads) is

$$k = Pd^2/4L, \quad (5)$$

where P is the total weight of the suspended system, d the distance between the threads, and L their length.

The bifilar suspension is exceptionally convenient for similar apparatus, because of the simplicity of its construction (a loop of thin wire was freely slipped on two hooks, one attached to a section of the instrument and the other to the suspended system), the excellent time-stability of the modulus and of the "null," its noncritical nature with respect to large angles of twist and strong overloading, and the possibility of using two current conductors.

The magnetic field was produced by an electromagnet with which it was possible to obtain in a 25-mm gap a field of about 5000 oe using a maximum current of 20 amp. The diameter of the pole pieces was 50 mm, and the angle of taper $\sim 40^\circ$. The field was calibrated by the usual ballistic method.

The measurement precision of the absolute values of the susceptibility was 7%, of the anisotropy $\sim 1.5\%$ (a little worse for tin); the precision of the relative measurements was not worse than 0.5 to 1%.

The specimens were cooled with liquid CH_4 , O_2 , N_2 , and H_2 ; a temperature of 64°K was obtained by pumping out the vapor above liquid nitrogen.

EXPERIMENTAL RESULTS

We have investigated the principal values of the susceptibility tensor of single crystals of In, Pb, and Sn in the above-mentioned temperature range. The corresponding values at room temperature are listed in the Table along with data of other authors from the literature.

(a) Indium. The temperature dependence of the magnetic susceptibility of indium is most typical for the majority of the elements belonging to the group of interest. The measured values of $\chi_{\perp}(T)$ and $\Delta\chi(T)$ of two specimens were in full agreement. The values of $\chi_{\perp}(T)$ and the calculated $\chi_{\parallel}(T)$ are shown in Fig. 2. χ_{\perp} increases by 20% as the temperature decreases from room temperature to 80°K , then, after passing through a maximum, it decreases; at $T = 20.4^\circ\text{K}$ it exceeds the value at room temperature by 15%. χ_{\parallel} increases monotonically up to 20°K by almost a factor of 3, and has a point of inflection at $T \sim 100^\circ\text{K}$.

(b) Lead. The $\chi(T)$ and the anisotropy in the (110) plane of two lead specimens which showed excellent agreement were investigated. The susceptibility increases almost linearly with de-

Metal	Author and year of measurement	$\chi_{\parallel} \cdot 10^6$	$\chi_{\perp} \cdot 10^6$	$\Delta\chi \cdot 10^6$	Remarks
In	Verhaeghe, ¹² 1950	0.1215	0.0545	0.067	$\delta = 1,6 \cdot 10^{-3}$ Precision $\sim 15\%$
	Verkin, ¹³ 1950	—	—	0.107	
	Schoenberg, ¹⁴ 1952	—	—	0.096	
	Present work	0.158	0.078	0.080	
Pb	deHaas and van Alphen, ¹⁵ 1933	0.111	—	—	
	Rao, ¹⁶ 1936	0.107	—	—	
	Present work	0.114	—	—	
Sn	Hoge, ¹⁷ 1935	0.0241	0.0270	0.0029	Polycrystal
	Itterbeek, ¹⁸ 1957	0.026	—	—	
	Present work	0.026	0.029	0.0029	

creasing temperature down to 20.4°K by 20% (cf. Fig. 2); there is no anisotropy.

(c) Tin. Tin is unusual in the investigated group in that it has a positive susceptibility, and it was therefore interesting to find out whether it obeys the basic rules characteristic of this group as a whole. The results of reference 18 indicating a decrease of the susceptibility of tin with decreasing temperature are only of qualitative nature, since they cannot be related to given crystallographic axes.

We have studied the values of $\chi_{\perp}(T)$ along the normal to the (010) plane and $\Delta\chi(T)$ in the (100) plane. The obtained curve, and the calculated $\chi_{\parallel}(T)$ curve for a tin crystal are shown on Fig. 2. Unlike other elements, the absolute value of the susceptibility of tin decreases with decreasing temperature. A linear decrease of χ_{\parallel} by 6% is observed down to 20.4°K, χ_{\perp} decreases by 15%, but has a deflection towards the temper-

ature axis (this is better seen in the temperature dependence of the anisotropy).

DISCUSSION OF THE RESULTS

The theory of the temperature dependence of the susceptibility which assumes that there exists one group of electrons with a quadratic dispersion law, yields the following expression for χ_{el} :^{19,20}

$$\chi_{el} = \chi_0 f(T), \quad (6)$$

$f(T)$ is a universal temperature function with the following asymptotic behavior:

$$\begin{aligned} T \ll E_0/k, \quad f(T) &= 1 - (\pi^2/12) (kT/E_0)^2, \\ T \gg E_0/k, \quad f(T) &= 2E_0/3kT. \end{aligned} \quad (7)$$

χ_0 has the form:

$$\chi_0 = (\sqrt{2} e^2 / 6c^2 h \pi) \sqrt{E_0/m^*} [3(m^*/m)^2 - 1], \quad (8)$$

where E_0 is the limiting energy, m is the mass of the free electron, m^* is its effective mass. The majority of the experimental $\chi(T)$ curves of the investigated elements (Figs. 2 and 3) can be described by the above formula if it is assumed that the limiting energies and effective masses of the electrons are anomalously small. The almost complete temperature independence of χ along some crystallographic directions in Cd, In, Sb, and C is apparently connected with the sharp anisotropy of the effective masses. These assumptions are in good agreement with the investigations of the de Haas—van Alphen effect.

Zil'berman and Itskovich²⁰ found the dependence $\chi(T)$ for cases where together with a small electron group there exists (a) a large electron group or (b) a large group of electrons and a large group of holes. The shapes of the curves are quite diverse; in particular, one can obtain a curve similar to the experimental curve obtained for Zn. However, near the temperature of degeneration of the small group, the form of the $\chi(T)$ curve is

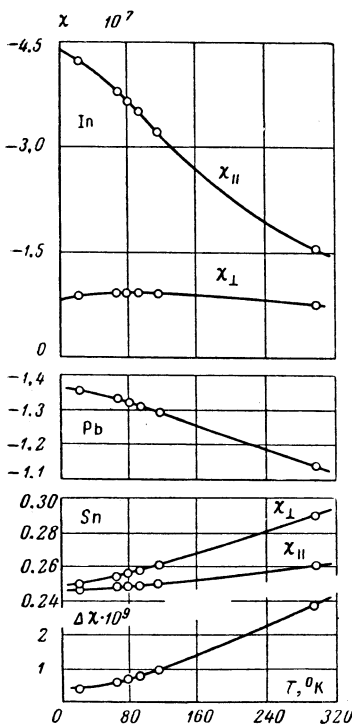


FIG. 2. Temperature dependence of the magnetic susceptibility of In, Pb, and Sn.

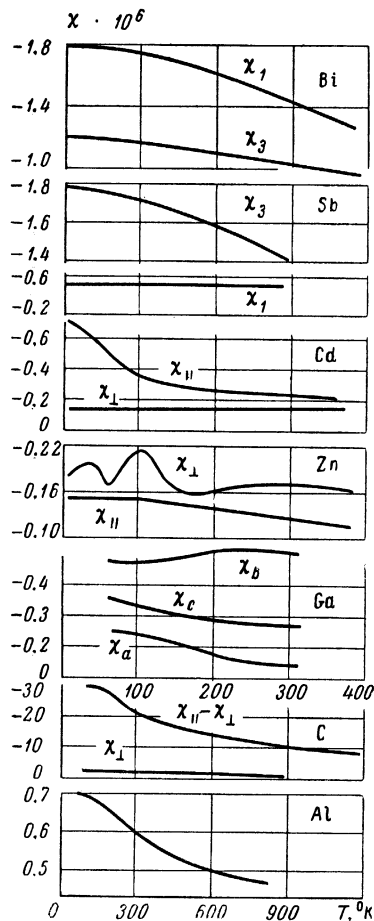


FIG. 3. The temperature dependence of the magnetic susceptibility of other elements in the investigated group (from the literature)

determined, as before, by the contribution due to this group.

The decrease of the absolute value of the susceptibility of tin with decreasing temperature can be explained either by the influence of the group of holes, or by the increase of the diamagnetism of the small electron group on a background of an anomalously large paramagnetic contribution of the main group, which is almost temperature independent in the investigated region. An unambiguous answer is possible on the basis of more complete information on the number and parameters of the groups of charge carriers, such as was obtained, for instance, from studies of the de Haas—van Alphen phenomenon. Making use of such data and of the corresponding theoretical relations, it was possible to plot $\chi(T)$ curves, and by comparing them with the experimental curves, to improve the precision of the zone structure and divide the groups into electrons and holes. However, the insufficient information makes a detailed quantitative comparison of theory and experiment difficult, and is one of the reasons of the discrepancy between them. Thus, the limiting energies of small groups of indium and cadmium

found from the quantum oscillations of the values of χ (reference 14) exceed by more than a factor of 20 the values obtained from the $\chi_{\parallel}(T)$ curves (the limiting energy approximately corresponds to the point of inflection of the curve). The typical “electron” increase of paramagnetism with decreasing temperature in Al (reference 21) cannot be reconciled with the small effective mass of 0.08 m (reference 14), in spite of the fact that the agreement of the limiting energies (for the smaller groups) is good. Possibly the long-period oscillations of χ corresponding to these small groups have not been observed, and more careful studies of these elements are essential. The theory of the temperature dependence of the susceptibility is likewise in need of further development, since the quadratic dispersion law is in the majority of cases not even applicable to the small groups. Unfortunately, the possible peculiarities of the temperature dependence of χ , connected with the open Fermi surfaces of many metals of interest to us,²² have as yet not been clarified.

Considering the nature of the anomalous groups, attention should be directed to the crystallochemical structure of the elements in the periodic table.^{2,23} Here it is easy to follow the gradual transition from the purely metallic bonding forces on the left to the molecular forces in the crystals of the noble gases. Thus, the highly-compressible cubic structures of the so-called “ideal” (alkaline) metals are due to isotropic metallic bonds; the transition metals are characterized by an additional admixture of d -electron shells. The group of elements which exhibits the long-period de Haas—van Alphen effect is characterized by the largest diversity of simultaneously present types of bonding forces. These are mainly the layer-like (graphite, Bi, Sb, and As) and complex hexagonal (Be, Zn, and Cd) structures; metallic and covalent bonds are present within the layers, and van-der-Waals, metallic, and various intermediate bonds of a still unknown nature are active between the layers. The lattices, it can be seen, are extremely anisotropic with a small compressibility because of presence of forces which are highly sensitive to the spacing. Even the most symmetrical of these elements — lead, indium, and tin — have anomalously large lattice periods which indicate the presence of additional nonmetallic forces. A consistent account of the complex interactions in the lattices may possibly offer a natural explanation of the separation of the small charge-carrier groups.

The study of the temperature dependence of the

susceptibility can serve as valuable supplementary information on the structure of the electron spectrum of the metals having such anomalous groups.

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