MAGNETISM OF CONDUCTION ELECTRONS OF NON-TRANSITION MULTIVALENT METALS

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Comparison of the temperature dependence of the magnetic susceptibility with the theory of the Landau-Peierls contribution shows that the latter does not describe the experimental data for multivalent non-transition metals. The magnetism of these metals is successfully explained on the basis of qualitative ideas regarding the contribution of interband interactions. In particular, the predicted temperature dependence of the susceptibility of a two-band model explains all the experimental variations of it in pure metals and alloys, in good agreement with the peculiarities of electronic structure of the latter.

DISCUSSION of experimental data on the orbital magnetic susceptibility of conduction electrons has usually taken the form of a comparison with the theory of the well-known Landau-Peierls contribution, χ_{LP}, which is a consequence of the quantization of the orbital motion of electrons in a magnetic field. A complete theoretical calculation of the susceptibility, recently developed,[1] gave a term additional to χ_{LP}, due to interaction between states in different bands. As follows from the work of Adams,[2] in which an estimate of this term χ_A was first given for a two-band model, it can become as large as χ_{LP} if the energy gaps at the edges of the bands are sufficiently small. It is at present impossible to obtain more information from the exact results of the work,[1] because the electronic Bloch wave functions that occur there are unknown.

It is of interest to review the existing experimental data on orbital magnetism, with allowance for the term χ_A, in order to elucidate its role and characteristic peculiarities. The most suitable objects for this purpose are, in our judgment, the multivalent non-transition metals, whose electronic structure is favorable for the appearance both of χ_{LP} and of χ_A. In fact, the energy gaps at the faces of the Brillouin zones are small,[3] and multiple intersections of the faces by the Fermi surface lead to the occurrence of electron and hole states with small limiting threshold energy ($E_0 \sim 0.01$ eV) and small effective mass ($m^* \sim 0.01\, m_0$).[4] These states, in addition to a long-period de Haas-van Alphen effect, should give an enhanced Landau-Peierls contribution ($\chi_{LP} \sim (E_0/m^*)^{1/2}$), with an unusual dependence on temperature near $T \approx 300°$ K.[5] The problem of the proposed work is to show the insufficiency of the Landau-Peierls theory by a comparison of the predicted $\chi_{LP}(T)$ dependence with the experimental results, and to give a qualitative interpretation of the latter on the basis of the term χ_A. It should be mentioned that a detailed study of the magnetic properties of alloys of bismuth[6,7] and indium[8] demonstrated the dominant role of the term χ_A in these metals; we have nevertheless included them in our comparison with the χ_{LP} theory, in order to emphasize the consistent nature of the deviations from it among all the multivalent metals.

1. COMPARISON WITH THE LANDAU-PEIERLS THEORY

Experimental investigation of the temperature dependence of χ for pure non-transition metals is essentially complete. Figure 1 presents collected data, taken from a similar review,[9] supplemented by the following works:[10] (Cu, Ag, Au),[11] (Be),[12] (Mg, Ca, Tl),[4] (Hg),[13] (Sr),[14] (Ba),[15] (As). For zinc below $T \sim 100°$ K, the dependence of χ on the value of the magnetic field H is given; the curves presented, on the basis of the data of [16,17], correspond to $H \to 0$. For the alkali metals there is no appreciable dependence of χ on T.

Metals with valence $Z \gtrsim 2$ show a long-period de Haas-van Alphen effect and an appreciable dependence of the monotonic part of the susceptibility on temperature, in qualitative agreement with the

Landau-Peierls theory. Furthermore, the form of the $\chi(T)$ curves in a number of cases (for example, Be, Cd, Al, In, Tl, Bi, and Sb) resembles that predicted by the theory enough to produce the illusion of full agreement with it. We shall attempt to carry out for the metals enumerated a semiquantitative comparison with the Landau-Peierls theory, by superposing the actual $\chi(T)$ dependences and the $\chi_{LP}(T)$ curve for a single isotropic parabolic band, as was done in [8] for In. The superposition of the curves was accomplished by adjustment of the two parameters $T_0 = E_0/k$ and $\chi(0)$, the susceptibility at $T = 0$; then from these, according to the formula

$$\chi(0)_{\text{volumetric}} = -0.097[E_0 m_0 / m^*]^{1/2} \text{ erg}^{-1/2}$$

the value of m^* was calculated for the states responsible for the magnetism. The parameters thus obtained are given in the first part of the table (columns 2 and 3); the second part (columns 4 and 5) contains similar information from the quantum oscillation of the susceptibility,[4] confirmed by other investigations. It remains only to show

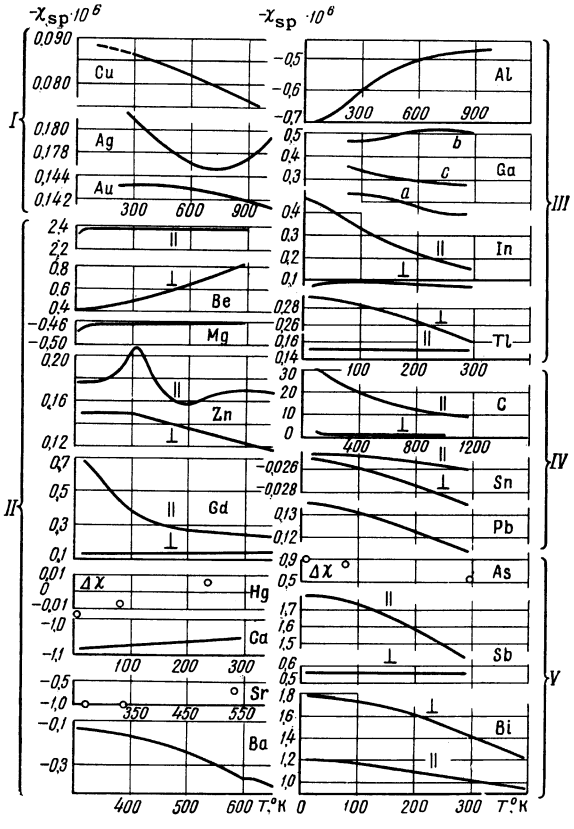

FIG. 1. Temperature dependence of the magnetic susceptibility of non-transition metals. The susceptibility in the direction of the crystallographic axis of highest symmetry is denoted by the symbol ||, perpendicular to it by the symbol $\perp$; $\Delta\chi \equiv \chi_{||} - \chi_{\perp}$; the Roman numerals indicate the valence of the metals. (χ_{sp} = specific susceptibility).

Metal	T_0, °K	$10^5 m^*/m_0$	T_0, °K	m^*/m_0
Be	500	5	600	0.03
Cd	100	0.5	1650	0.4
Al	680	<40	430	0.08
In	150	2	2100	0.3
Tl	380	18	800	0.35
Sb	480	1.0	1300	0.05
Bi	500	0.8	210	$2.5\cdot10^{-3}$

The last column gives the smallest values.

that the obvious absurdity of the consequences of an application of the Landau-Peierls theory is not due to the choice of a simplified model. An approach to real conditions increases the anomalousness of the calculated effective masses, according to the following principles.

First, in the majority of multivalent metals there also exist groups of electrons and holes with energy ~10 eV, which diminish the temperature modulation of the susceptibility.[5] Then the actual values of $\chi_{LP}(0)$ will exceed those found earlier, and m^* will decrease by one to two orders.[8]

Second, the minimum value of the effective mass proves to be even smaller, if we take into account its considerable anisotropy.

Third, it is found that the spin splitting of the levels in a magnetic field can be commensurate with the orbital, because of spin-orbit coupling,[18] and the Pauli paramagnetism can decrease or even completely absorb the Landau-Peierls diamagnetism. Both contributions to the susceptibility have the same form of temperature dependence of the modulus of the susceptibility (but different signs of $d\chi/dT$),[19,20] so that when account is taken of paramagnetism, the anomaly of the effective mass (whether spin or orbital) can only be aggravated. Furthermore, experiment qualitatively contradicts the picture under consideration, in that a "paramagnetic" sign of $d\chi/dT$ is observed in metals with negligible spin-orbit interaction (Al, Be[21]), and large diamagnetism and a positive sign of $d\chi/dT$ occur in metals with strong spin splitting (Sb[22], Bi[23]).

It is unlikely that such a profound and regular anomaly of m^* was caused by such irregular causes as non-parabolicity of the bands or temperature change of the structure of the spectrum, which can alter the $\chi_{LP}(T)$ dependence.[24] Evidently the Landau-Peierls contribution is in principle unsuited for description of the susceptibility of multivalent metals. It is necessary to turn to the mechanism revealed in their characteristic representatives, bismuth and indium: the more so, because the consequences of a comparison with the

Landau-Peierls theory are completely similar for them and for the other metals.

2. COMPARISON WITH THE THEORY OF INTERBAND INTERACTIONS

A rough quantitative estimate of the term χ_A has been obtained only for an electronic structure of the bismuth type.[2] From it, it follows that even the largest observed values of diamagnetism (Be, Bi, Sb) are described by this term with realistic values of m*. More convincing evidence of the dominance of χ_A is provided by the peculiar dependence on electron concentration, qualitatively predicted in [25]. In the two-band model mentioned (Fig. 2), the occupied states of the lower band give a diamagnetic, and of the upper band a paramagnetic, contribution to the susceptibility, because the magnetic field draws together states that are nearly degenerate, and the greatest role is played by states close to the extreme points of the bands.

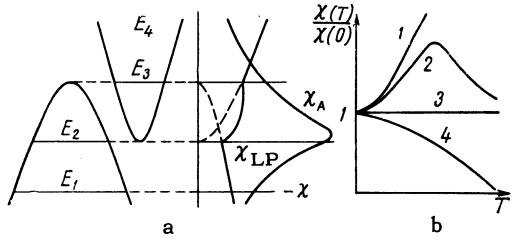

FIG. 2. a. Schematic dependence of χ_{LP} and χ_A on filling level in a two-band model. b. Expected behavior χ_A (T) for different fillings.

The corresponding character of the dependence of χ_A on the filling level is shown in Fig. 2 and, as is evident, contrasts sharply with the χ_{LP} contribution. Just such a behavior made it possible to identify the susceptibility of alloys of bismuth and indium (cf. Fig. 3, which shows the $\chi_\perp(Z)$ dependence of alloys of bismuth with tellurium and lead and the $\chi_\parallel(Z)$ dependence of alloys of indium with cadmium and lead; the value of the mean valence Z of the bismuth alloys takes account of the effectiveness of impurities[26]). The extrema of χ for these alloys mark the filling of special points of the zones; the bottom of the sixth zone for bismuth and the corners of the third zone for indium. Peculiarities in other properties are also observed, for example superconductive transition temperatures in the alloys of indium.[27][1)]

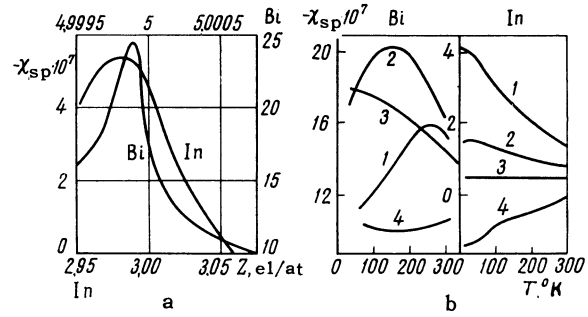

FIG. 3. Experimental dependence of the susceptibility of alloys of Bi and In: a, on electron concentration (at 78°K for Bi and at 20.4°K for In); b, on temperature; the sequence of the curves corresponds to increasing electron concentration: for the Bi alloys, 1 = +3.95 at. % Pb, 2 = +1.04 at. % Pb, 3 = pure Bi, 4 = +0.11 at. % Tl; for the In alloys, 1 = +0.5 at. % Pb, 2 = +3 at. % Pb, 3 = +5 at. % Pb, 4 = +10 at. % Pb.

Thus the form of the $\chi_A(Z)$ dependence has been established with sufficient certainty. Thermal excitation of the electrons may act analogously to a change of the filling level in pure metals, and we shall try to predict the form of the $\chi_A(T)$ curves qualitatively, using the known $\chi_A(Z)$ dependence. We return to Fig. 2 and consider the behavior of $\chi_A(T)$ when the filling level is E_1. With increase of temperature, there occurs a filling of states near the extremum of the lower band; and in accordance with $\chi_A(Z)$, the diamagnetism increases (curve 1 of the right part of the figure). When $kT > E_2 - E_1$, the $\chi_A(T)$ dependence should have a maximum (curve 2), since the paramagnetic states at the bottom of the upper band begin to be filled. On increase of the filling level to E_2, the maximum of the $\chi_A(T)$ curve should move to T = 0, and the descending branch of it remains (curve 4). If the filling level exceeds E_3, then with increase of temperature the paramagnetic states at the bottom of the higher band are released, and the diamagnetism again increases (curve 1). Near E_3, where the sign of $d\chi/dT$ changes, the susceptibility should not depend on temperature (curve 3).

From Fig. 3b it is clear that the contribution χ_A unconstrainedly explains not only the actual $\chi(T)$ dependence of the alloys of bismuth (in which, by the way, all forms of the $\chi(T)$ dependence of pure non-transitional metals are realized), but also its sequence of forms upon change of the electron concentration. The specific behavior of $\chi_A(T)$ is determined by the relative distribution of the states that take part in interband transitions, the number of bands, and the value of the contribution (anisotropic to the degree that m* is anisotropic) of each of them to the susceptibility. It is therefore possible to relate a peculiarity of form of the

[1)]The authors are grateful to M. Merriam for acquainting them with the communication [7] before its publication.

experimental $\chi(T)$ curve to a peculiarity of the electronic structure of the metal only in the simplest cases, like bismuth. Thus in aluminum the basic role is apparently played by states of one (the third) band, which form small swellings of the Fermi surface near the corners,[28] corresponding to a local minimum of the energy. With increase of temperature, these paramagnetic states are released, and the diamagnetism increases (cf. Fig. 1). If, by introducing into the aluminum an impurity of lower valence, we decrease the electron concentration enough so that the states mentioned are completely vacated, a change of sign of $d\chi/dT$ should occur. Actually, upon introduction of 3.6 atomic percent Mg[29] the sign does change; and an extrapolation of the data of reference[30] shows that just at this concentration of a bivalent impurity (~ 3.5 at. %) the bulge of the Fermi surface contracts to a point.

A similar effect of change of sign of $d\chi/dT$ is observed in a number of bivalent metals of hexagonal structure, with increasing ratio of periods c/a: Be, Mg, Zn, Cd (Fig. 1). According to the almost-free electron model, increase of c/a is equivalent to decrease of the filling level for states parallel to the axis c of the zone edges. Small electron groups in the upper band disappear, and groups of holes appear in the lower; in consequence, just as in the aluminum alloys, the sign of $d\chi/dT$ changes. The ratio c/a in zinc is close enough to the critical value so that the change of electronic structure under consideration takes place with thermal expansion of the lattice,[31] and the curious $\chi_{\parallel}(T)$ dependence of this metal—the subject of many discussions[5, 16, 17, 24]—is a direct analog of $\chi_A(Z)$ (Figs. 2 and 3a). The maximum of the diamagnetism at $T \approx 110°K$ should correspond to disappearance of an electron group; this is confirmed by the abrupt decrease of the corresponding section of the Fermi surface on increase of temperature.[17]

Thus the magnetic susceptibility of multivalent non-transition metals can be successfully interpreted on the basis of qualitative ideas regarding the contribution of interband interactions; these explain not only the order of magnitude of the susceptibility, but also all the forms of its temperature dependence. Peculiarities of the electronic structure of metals and alloys, determined from the peculiarities of behavior of the magnetic susceptibility, are in good correspondence with results of direct investigation. All that has been said allows us to conclude that it is the contribution of interband interactions that is dominant in non-transition metals.

It may be expected that this contribution will play a significant role in univalent metals, especially in those whose Fermi surfaces "sense" the proximity of an edge of a Brillouin zone, and also in transition metals. In particular, experimental estimates of the diamagnetism of lithium reveal an appreciable deviation from the Landau-Peierls theory;[32] and the appreciable $\chi(T)$ dependences of copper, silver, and gold look more like the χ_A term. Definitive conclusions for these metals, however, are still far off.

CONCLUSION

The work reported is an attempt to comprehend the accumulated experimental material on the magnetism of the non-transition metals; but it contains it in sufficient quantity to justify, in the authors' opinion, a conclusion regarding the dominance of the contribution from interband interactions. We have omitted the results of a number of interesting investigations; in particular, of γ-phase alloys of copper, which also agree with the χ_A theory. That theory requires further development. Although the qualitative explanation of the $\chi_A(T)$ dependence proposed in this work also permits utilization, to some degree, of the existing data for the purposes of spectroscopy, it is quite insufficient for a complicated band structure. Thus the change of sign of $d\chi/dT$ in alloys of indium (Fig. 3b), which with respect to electronic structure are close to alloys of aluminum, cannot be successfully related to the filling of specific states, because various states of many near-lying bands participate in the effect.[8] There is need for a rigorous quantitative calculation of the value of the χ_A contribution, and for establishing a clear connection between the peculiarities of its behavior and the character of the electronic structure. As is evident from the preceding section, the magnetic susceptibility can give information about the change of fine details of the spectrum under the influence of temperature or of impurities, which is inaccessible by most other methods. A basic aim of our article is to attract the attention of theorists to this valuable property of the magnetic susceptibility, which compensates for the great labor of calculating it.

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