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Temperature Dependence of the Magnetic Susceptibility of Electrons in Metals

G. E. ZIL'BERMAN AND F. I. ITSKOVICH (Submitted to JETP editor May 28, 1956) J. Exptl. Theoret. Phys. (U.S.S.R.) 32, 158-160 (January, 1957)

W E have investigated the temperature dependence of the magnetic susceptibility x of electrons over a wide range of temperatures in weak magnetic fields, where x is practically independent of H. The necessity of this investigation for the classification of magnetic materials was pointed out to us by Verkin¹. The following cases were studied: 1) only small groups of electrons are present; II) there is, in addition to these small groups, a large group of electrons; III) besides the foregoing there is a large group of holes. The calculation is carried out for a quadratic law of dispersion with respect to the spin paramagnetism and to the anisotropy of the effective masses.

We consider hexagonal crystals like bismuth (for other types of symmetry the results do not differ qualitatively). We make the usual assumption that these crystals have three identical small groups in the form of ellipsoids, the axes of which make an angle of 120° in the plane of the binary axes.

Case I. Carrying out our calculations as in Refs. 2 and 3, we obtain the component x_i (3 is the index of the principal axis) of the three groups referred to:

$$\chi_{i} = -\frac{1}{2}AB_{i}(kT)^{1/2}F_{-1/2}(\zeta / kT) = -AB_{i}V\overline{\zeta_{0}}X \quad (1)$$

(since $m_i \ll m_0$, where m_0 is the mass of a free electron, we can ignore the spin paramagnetism). In this equation,

$$A = V \overline{2} e^{2}/6\pi hc^{2}, B_{1} = B_{2}$$
(2)

$$= 3 (m_1 + m_2)/2V \overline{m_1 m_2 m_3}$$
, $B_3 = 3m_3/V \overline{m_1 m_2 m_3}$

$$\chi = \frac{1}{2} \sqrt{\theta} F_{-\frac{1}{2}}(u);$$
 (3)

$$\theta = \frac{T}{T_0}, \ T_0 = \frac{\zeta_0}{k} , \qquad (4)$$

$$\zeta_0 = \zeta |_{T=0} = \left(\frac{nh^3}{16\pi \sqrt{2m_1m_2m_3}}\right)^{b/s};$$

$$F_s(u) = \int_0^\infty \frac{x^s dx}{1 + e^{x-u}}, \quad u = \frac{\zeta}{kT}.$$

The dependence of the chemical potential ζ on temperature is determined from the condition that the concentration n of electrons be constant, which gives

$$\theta = [{}^{3}/{}_{2}F_{{}^{1}/{}_{2}}(u)]^{-{}^{2}/{}_{3}}$$
(5)

By calculating the function $F_{\pm \frac{1}{2}}$, we determine from Eqs. (3) and (5) the function $X(\theta)$, which is the desired dependence X(T) in generalized c cordinates, and also $\zeta(\theta)/\zeta_0$. For the limiting cases – strong degeneracy and Boltzmann statistics – we obtain

$$T \ll T_{0}: X = 1 - \pi^{2} \theta^{2} / 12,$$

$$\zeta / \zeta_{0} = 1 - \pi^{2} \theta^{2} / 12;$$

$$T \gg T_{0}: X = 2 / 3\theta,$$

$$\zeta / \zeta_{0} = (3/2) \theta \ln [(16 / 9\pi)^{1/2} \theta^{-1}].$$
(3 ')

Curves of $X(\theta)$ and $\zeta(\theta)/\zeta_0$, and also their asymptotic expressions (broken curve), are presented in Fig. 1. A series of metals has just this temperature dependence for x.

Case II. The dependence of the chemical potential ζ' of a large group (we consider its ellipsoid of revolution with $m'_1 = m'_2 \sim m'_3 \sim m_0$) on T is represented here, as it turns out, by the same curve (Fig. 1) as in the preceding case (only the scale is changed; the new reduced temperature $\theta' = T/T_0'$, where $T_0' = \zeta'_0 / k$; generally $\zeta_0' >> \zeta_0$). From the definition of $\zeta(T)$ (for a small group) it turns out that the parameter $\alpha = \zeta_0 / \zeta_0' \leq 1$.

The overall magnetic susceptibility of the small (X_{α}) and large groups is equal to

$$\chi_i = -A \sqrt{\overline{\zeta_0}} \left[B_i X_\alpha \left(\theta' \right) + B'_i X \left(\theta' \right) \right], \tag{6}$$

$$B'_{1} = B'_{2} = 1 / \sqrt{m'_{3}} - 3m'_{1} \sqrt{m'_{3}} / m_{0}^{2}, \qquad (6)$$

$$B'_{3} = \sqrt{m'_{3}} / m'_{1} - 3m'_{1} \sqrt{m'_{3}} / m_{0}^{2},$$

$$X_{\alpha}(\theta') = \frac{1}{2} \sqrt{\theta'} F_{-1_{2}} \left[u'(\theta') - \frac{1 - \alpha}{\theta'} \right];$$

$$\theta = \frac{\theta'}{\alpha} \ll 1, \tag{7}$$

$$X_{\alpha} = V_{\alpha} \left[1 - \frac{\pi^2}{24} (1 + \alpha) \theta^2 \right]$$

Curves of $X_{\alpha}(\theta')$ are presented in Fig. 2. If $\alpha \ll 1, X_{\alpha}(\theta')$ has a minimum for $T \sim T_{0}$ and a weakly-expressed maximum for $T \sim T_{0}/2$; if $\alpha > \alpha_{0} \sim 0.2, X_{\alpha}(\theta')$ decreases monotonically, approach ing $X(\theta)$ for $\alpha \sim 1$. For $T \gg T_{0}', X_{\alpha}(\theta') = 2/3 \theta' = X(\theta')$.



For the sum of the two terms in (6) there are several possibilities, depending on the values of α and the effective masses (in particular, B_i ' can be negative), but for $T < T_0 << T_0$ ' the temperature dependence is determined principally by the small groups.

Case III. In this case the total number of particles increases with temperature, but $n_{el} - n_{holes} = \text{const}$ We shall take $n_{el} = n_{holes}$, which gives

$$\gamma^{3/2} F_{1/2}(u') = F_{1/2} \left(\frac{1+\gamma}{\theta'} - u' \right), \qquad (8)$$
$$\gamma = \left(\frac{m'_1 m'_2 m'_3}{m_1^0 m_2^0 m_3^0} \right)^{1/3}$$

Here there appears only a single parameter γ ; the mass $m_i^0 \sim m_0$ relates to the assembly of holes, which we also consider in terms of its ellipsoid of rotation around the principal axis. The condition (8) can give a qualitatively different dependence for $\zeta''(T)$ than (5). Namely, $\zeta'(T)$ can not only decrease ($\gamma > 1$), but also increase ($\gamma < 1$), and even stay identically constant ($\gamma = 1$), whereupon the law of the change of ζ' at low T is parabolic, as before;





The total magnetic susceptibility is now equal to:

$$\chi_i = -A \sqrt{\overline{\zeta_0'}} \left[B_i X_{x,\gamma} \right] (\theta')$$
(9)

$$+ B_i' X_{\gamma}'(\theta') - B_i^0 X_{\gamma}^0(\theta')],$$

where the B_i^0 are determined in the same way as the $B_i'(6')$;

$$X_{\alpha,\gamma}(\theta') = \frac{1}{2} V \overline{\theta'} F_{-\frac{1}{2}} \left[u'_{\gamma}(\theta') - \frac{1-\alpha}{\theta'} \right]$$
$$X'_{\gamma}(\theta') = \frac{1}{2} V \overline{\theta'} F_{-\frac{1}{2}} \left[u'_{\gamma}(\theta') \right], \qquad (10)$$
$$X^{0}_{\gamma}(\theta') = \frac{1}{2} V \overline{\theta'} F_{-\frac{1}{2}} \left[\frac{1+\gamma}{\theta'} - u'_{\gamma}(\theta') \right];$$

here $u'_{\gamma}(\theta')$ is a function determined from (8). For low T:

$$X_{\alpha, \gamma} = V\overline{\alpha} \left[1 - \frac{\pi^2}{24} \left(1 + \frac{\gamma - 1}{\gamma} \alpha \right) \theta^2 \right]$$
(10)

 $(T \ll T_0);$

$$X'_{\gamma} = 1 + \frac{\pi^2}{12} \frac{1 - 2\gamma}{2\gamma} \theta'^2;$$
 (10')

$$\mathbf{X}_{\gamma}^{\bullet} = V \overline{\gamma} \left(1 + \frac{\pi^2}{24} \frac{\gamma - 2}{\gamma^2} \, \theta'^2 \right) \quad (T \ll T_0').$$

(10) for $\alpha \ll 1$ agrees with (7); the function (10'), depending on γ , can also increase as well as decrease. For high T all three functions (10), and .consequently x_i as well (9), increase (for $T \gg T_0'$ they are proportional to \sqrt{T} , where upon $X_{\alpha\gamma} = X_{\gamma}$).

Several representive curves are presented in Fig. 1 for $(X_{\gamma}, X_{\gamma}^{\circ})$ and in Fig. 2 for $(X_{\alpha\gamma})$. For the sum of these curves (with corresponding coefficients) the various possibilities are even more numerous than in Case II. In particular, one can obtain a curve containing several maxima, similar to the experimental curve of Verkin (4) for Zn. For $T < T_0 \ll T_0'$ the small groups give the basic tem-

perature dependence, as before.

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Contribution to the Thermodynamical Theory of Ferroelectrics

I. A. IZHAK

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F ROM the thermodynamical theory of ferroelectrics developed by Ginzburg^{1,2}, there follows a series of important conclusions concerning the dependence of the dielectric properties of barium titanate on mechanical stress. Strictly speaking, the theory applies only to single-domain monocrystals; however, in the paraelectric region it is expedient to attempt to compare experimental data obtained for polycrystals with the conclusions of the theory. Below we present data which we have obtained for polycrystalline samples of BaTiO₃, which corroborate certain conclusions of the thermodynamical theory.

1. The expansion of the thermodynamical potential Φ in the presence of an elastic stress σ_{ik} differs from the analogous expansion in the absence of a stress only in the coefficients α_i for the polarization p_i^2 ^{3,4}. If there exists only a single compression, along the *x*-axis, for instance, then for the parallel and perpendicular directions we have respectively:

$$\alpha_1 = \alpha - \varkappa_1 \sigma_{xx}, \quad \alpha_2 = \alpha - \varkappa_2 \sigma_{xx}, \quad (1)$$

where κ_1 , κ_2 are the strain coefficients, and α the expansion coefficient in the absence of compression.

It is possible to determine the coefficients α_1 and α_2 from measurements of the dielectric constant:^{1,4}

$$\alpha_1 = 2\pi / \varepsilon_{xx}, \quad \alpha_2 = 2\pi / \varepsilon_{yy} \quad (T > \Theta).$$
 (2)

In Fig. 1 is shown the experimental behavior of the coefficient α_1 as a function of pressure (unilaterally applied) for various temperatures above the Curie point, calculated from our measurements of the dielectric permittivity for polycrystalline BaTiO₃ in a weak field (7 volts/cm) at high frequency (1 Mc/s). It is clear that the linear dependence of α_1 on unilateral pressure, as required by the theory, is well realized over a wide range of pressure, in which

$$\varkappa_1 \approx + 0.75 \cdot 10^{-12} \,\mathrm{cm}^2/\mathrm{dyne}$$
 (3)

For measurements of ϵ in the direction perpendicular to the axis of compression, the linear dependence is violated for pressures beyond 500 kg/cm², but in the region where linearity is preserved,

$$\varkappa_2 \approx -0.23 \cdot 10^{-12} \text{ cm}^2/\text{dyne}$$
 (4)

The values (3) and (4) are smaller than the estimates based on x-ray measurements and the temperature dependence of the spontaneous polari-