Anomalous temperature dependence of the magnetic susceptibility of beryllium

G. E. Grechnev, I. V. Svechkarev, and Yu. P. Sereda

Physicotechnical Institute of Low Temperatures, Ukrainian Academy of Sciences
(Submitted 3 March 1978)
Zh. Eksp. Teor. Fiz. **75**, 993–999 (September 1978)

The temperature dependence of the magnetic susceptibility of single-crystal beryllium is investigated in the temperature interval 4.2–1500 K and is theoretically interpreted. An anomalously high maximum of the diamagnetism is observed in the basal plane at $T = 870$ K and is due to the approach of the chemical-potential level to the point of band degeneracy on the line Σ. The temperature-induced changes of the parameters of the beryllium spectrum near the band degeneracy point and the corresponding dependences of the susceptibility on the chemical-potential levels are calculated for various temperatures in a model with a nonlocal psuedopotential and an isotropic Debye-Waller factor. Comparison of these calculations with experiment yielded the position of the chemical potential level relative to the degeneracy point in the interval $500 < T < 1300$ K.

PACS numbers: 75.30.Cr

I. INTRODUCTION

In a preceding paper[1] we calculated the orbital contribution to the susceptibility of beryllium from weakly split states located near the Fermi level. The calculation results explained qualitatively the main properties of the susceptibility of beryllium. It was established that the anomalously high diamagnetism along the hexagonal axis (the $\chi_\perp$ component) is due to large cigar-shaped groups of electronic states of the third band and depend little on the level of the chemical potential and on the temperature. The component $\chi_\perp$ is determined by the states of the necks of the hole "coronet" near the crossing of the levels Σ_1 and Σ_3 on the symmetry line Σ. (For the sake of brevity, we call this degeneracy point the critical point Σ and reckon from it the local value of the chemical potential μ_Σ.) At $T = 0$ K and at small μ_Σ the diamagnetism has a singularity of the type $\chi_\perp \sim |\mu_\Sigma|^{-1/2}$ and can exhibit a substantial dependence on the temperature.

A preliminary analysis of the experimental data[2] has shown that when the temperature increases to 300 K the level of the chemical potential approaches the critical point Σ.[1] One could expect further increase of the temperature to lead to a corresponding singularity in the susceptibility and describe more precisely the character of the behavior of the chemical-potential level. In the present paper, which is devoted to a realization of this program, we report an experimental and theoretical investigation of the properties of the magnetic susceptibility of beryllium in the temperature range from 4.2 to 1500 K.

II. PROCEDURE AND EXPERIMENTAL RESULTS

The magnetic susceptibility of single-crystal beryllium (~99.99% pure) was measured on the same samples as in the preceding study[2] by the Faraday method in fields 5–15 kOe produced by an SP-47 electromagnet. To measure the force acting on the sample in an inhomogeneous field we used a microbalance with electrodynamic automatic compensation of the load and with a capacitive displacement pickup (devices of similar construction[3] are widely used in magnetic investigations).

The oriented sample was securely mounted on quartz filament of 0.3 mm diameter with a quartz holder or with an annealed tantalum wire of high purity, and was suspended to the balance beam by a tube with a sealed bottom. The chamber with the balance and the tube were evacuated and filled with spectrally pure helium gas for heat exchange. In the lower part of the tube was placed a massive metallic block 100 mm long and with inside diameter 8 mm; it served to equalize and stabilize the temperature, which was measured with a thermocouple placed in the central part of the block. The sample was placed at the same level inside the block.

In the instrument for the low-temperature investigations (4.2–300 K) we used a thin-wall tube of stainless steel, a copper block, a Cu–Au + 1 at.% Fe thermocouple and a copper-constantan thermocouple, and the pressure of the heat-exchange gas was ~30 Torr. The tube with the block and sample was placed in an ordinary cryostat, and the measurements were made with the cryostat temperature rising slowly and in natural fashion from 4.2 K (rate of heating ~1 degree per minute).

In the instrument for the high temperatures (300–1500 K) we used a tube of quartz, a block of molybdenum, a chromel-alumel thermocouple, and a helium pressure ~0.1 Torr. To purify the heat-exchange gas, an adsorption carbon pump was permanently connected to the system and was cooled with liquid nitrogen. The sample temperature was regulated with an oven that a bifilar winding of nichrome wire of 1 mm diameter fed with direct current (to prevent mechanical interactions with the electromagnet field). The outer screen of the oven was cooled with running water and prevented heating of the pole pieces. In both instruments, the relative error in the measurement of the susceptibility did not exceed ±1%, the absolute error ±2%, and the sample-temperature error ±1%.

At temperatures above 1300 K, sublimation of the beryllium set in, but not enough to change noticeably

 0038-5646/78/090502-04$02.40

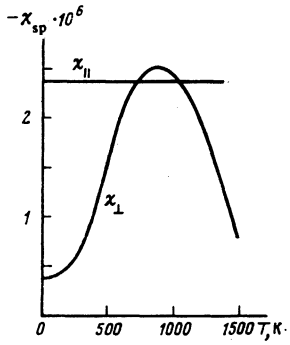

FIG. 1. Dependence of the components of the tensor of the specific magnetic susceptibility of beryllium on the temperature (in cgs specific units).

the mass of the sample during the minimal measurement time in this temperature region.

The temperature dependence of the magnetic susceptibility of beryllium is shown in Fig. 1. In the interval 4.2–300 K it coincides with the results of the preceding study.[2] With further increase of temperature, up to the point of the polymorphic transition of α-Be ($T = 1527$ K, Ref. 4), the anomalous diamagnetism of the component $\chi_\parallel$ retains its value. The component $\chi_\perp$, on the contrary, increases in absolute value, exceeds the $\chi_\parallel$ component, and reaches at 870 K a specific-diamagnetism maximum of record value for metals, after which it drops to almost its initial value. There is no doubt, in view of the results of Ref. 1, that the observed temperature anomaly of $\chi_\perp$ in beryllium is due to the approach of the chemical-potential level to the level degeneracy point. We consider below the structure of the spectrum and the expected behavior of the orbital susceptibility of the states near this point.

III. MODEL OF ENERGY SPECTRUM

States in the immediate vicinity of the crossing point of the levels Σ_1 and Σ_3 are described in the Luttinger–Kohn representation are described by a two-band Hamiltonian of the type

$$\mathcal{H} = \begin{pmatrix} Lk_z^2 + Ak_y & Qk_z \\ Qk_z & Lk_z^2 - Ak_y \end{pmatrix}. \tag{1}$$

The components k_x, k_y, and k_z of the wave vector are reckoned from the point Σ and correspond to the directions $[2\bar{1}\bar{1}0]$, $[01\bar{1}0]$, $[0001]$ in the Brillouin zone; A, Q, and L are the constants of the spectrum. Since we are interested in the states in a small vicinity of the singular point of the spectrum, we have left out of (1) the terms quadratic in k_i in the presence of the corresponding linear ones. Strictly speaking, the degeneracy of the levels Σ_1 and Σ_3 is lifted by the spin-orbit interaction, but the negligible value of the splitting ($\sim 10^{-5}$ Ry) allows us to neglect this splitting under real conditions.

For a correct calculation of $\chi_\perp(T)$ in a wide range of temperatures it is necessary to take into account the changes produced in the parameters of the spectrum in the Hamiltonian (1) by the thermal expansion and by the lattice vibration.[5,6] The published calculations of the band structure of beryllium[7-9] make it possible to determine only one constant, A, as $T \to 0$ K. To obtain all the constants of the Hamiltonian (1) in the required temperature interval, a calculation was made of a fragment of the beryllium band structure in the vicinity of the symmetry point Σ by the nonlocal-pseudopotential method. The matrix element of the Hamiltonian was chosen in the plane-wave representation in the form[7]

$$\langle \mathbf{k}_i | H | \mathbf{k}_j \rangle = k_i^2 \delta_{ij} + \delta_{\mathbf{k}_i - \mathbf{k}_j, G} S_\tau(G) \times \left\{ v(G) + [E(\mathbf{k}) - E_{1s}] \frac{\langle \mathbf{k}_i | 1s \rangle \langle 1s | \mathbf{k}_j \rangle}{\langle 1s | 1s \rangle} \right\}, \tag{2}$$

where $G = [h,\ k,\ h+\overline{2k},\ l]$ is the reciprocal-lattice vector. The data of Ref. 10 were used on the energy level E_{1s} and on the corresponding atomic wave function $|1s\rangle$. The form factors of the local part of the pseudopotential $v(G)$ were taken from Ref. 7, with allowance for the temperature dependence of the lattice constants.[11]

At finite temperatures, the structure factor in (2) is given by (see Ref. 6)

$$S_\tau(G) = \exp[-W(G, T)] \cos\{2\pi[{}^1/_6(h+2k) + {}^1/_4 l]\}, \tag{3}$$

where e^{-W} is the Debye-Waller factor:

$$W(G, T) = \frac{1}{2} \sum_{q, s, b} \frac{\hbar (2\bar{n}_{qsb} + 1)}{2MN\omega_{qsb}} |(G e_{qsb})|^2, \tag{4}$$

M is the ion mass, N is the number of unit cells in the crystal, ω_{qsb} is the dispersion law for the phonon mode with polarization s (the subscript b makes it possible to distinguish between acoustic and optical modes), $\mathbf{e}_{qsb}$ is the polarization vector, and $\bar{n}_{qsb}$ is the Bose-Einstein distribution function.

In the approximation where the Debye-Waller factor is isotropic

$$W(G, T) = D(T) G^2 \tag{5}$$

we obtain

$$D(T) = \frac{\hbar V_0}{48\pi^3 M} \sum_{s, b} \int dq \frac{(2\bar{n}_{qsb} + 1)}{\omega_{qsb}}, \tag{6}$$

where V_0 is the volume of the unit cell. The numerical integration in (6), using the experimental data on the phonon spectrum of the beryllium, yields the $D(T)$ dependence shown in Fig. 2.

The energy $E(\mathbf{k})$ of the levels Σ_1 and Σ_3 in the region of their crossing was obtained for various temperatures from the secular equation

$$|H - \delta_{ij} E(\mathbf{k})| = 0 \tag{7}$$

using 12 plane waves and the information reported above. The obtained spectrum fragments were then used to determine the parameters of the truncated Hamiltonian (1); their temperature dependences are shown in Fig. 3.

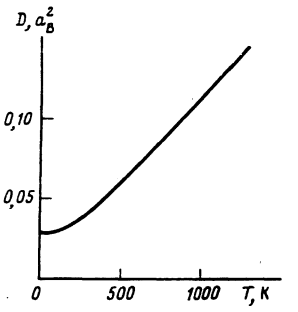

FIG. 2. Temperature dependence of the exponential coefficient of the Debye-Waller factor.

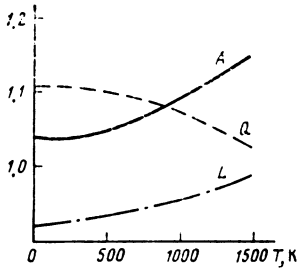

FIG. 3. Dependence of the constants of the spectrum of the model Hamiltonian on the temperature. The constants are given in atomic units: A (Ry·a_B), Q (Ry·a_B), L (Ry·a_B^2).

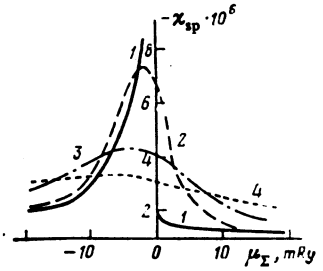

FIG. 4. Dependence of the component $\chi_\perp$ of the orbital susceptibility of beryllium on the chemical-potential level at temperatures 4.2 (1), 300 (2), 900 (3), and 1500 K (4).

IV. CALCULATION OF THE ORBITAL CONTRIBUTION TO $\chi_\perp$

The general formula for the orbital magnetic susceptibility of a multiband system of noninteracting Bloch electrons in a weak magnetic field is of the form[13]

$$\chi=\left(\frac{e\hbar}{c}\right)^2\frac{k_BT}{(2\pi)^3}\sum_{n=-\infty}^{\infty}\int d\mathbf{k}\,\mathrm{Sp}(\gamma^x g\gamma^y g\gamma^x g\gamma^y g). \tag{8}$$

Here χ is the component of the susceptibility tensor (per unit volume) along the z axis; γ^i are the matrices of the momentum components, calculated in the same representation as the initial Hamiltonian $\mathscr{H}$, and g is the Matsubara Green's function:

$$g=[i\pi k_BT(2n+1)+\mu-\mathscr{H}]^{-1}, \tag{9}$$

where μ is the chemical potential and k_B is the Botzmann constant. The integration in (8) is over the Brillouin zone.

For the Hamiltonian (1) we have in the limit as $T\to 0$ K the following components of the orbital contribution to the components of the magnetic-susceptibility tensor:

$$\chi_x^z=-\frac{3e^2AQ}{64\pi^2\hbar^2c^2Lk_z}\frac{1}{|\varepsilon|^{1/2}}\operatorname{arctg}\left(\frac{1}{|\varepsilon|^{1/2}}\right),\quad \mu_z<0,$$
$$\chi_x^z=-\frac{3e^2AQ}{64\pi^2\hbar^2c^2Lk_z}\frac{1}{\varepsilon^{1/2}}\ln(1+\varepsilon^{1/2}),\quad \mu_z>0, \tag{10}$$

$$\chi_y^z=-\frac{e^2QLk_z}{2\pi^2\hbar^2c^2A}\left(1-|\varepsilon|^{1/2}\operatorname{arctg}\left(\frac{1}{|\varepsilon|^{1/2}}\right)\right),\quad \mu_z<0,$$
$$\chi_y^z=-\frac{e^2QLk_z}{2\pi^2\hbar^2c^2A}\left(1-\frac{\varepsilon^{1/2}}{2}\ln\left|\frac{\varepsilon^{1/2}+1}{\varepsilon^{1/2}-1}\right|\right),\quad \mu_z>0, \tag{11}$$

where $\varepsilon=\mu_\Sigma/Lk_\Sigma^2$, and k_Σ is the limit of applicability of the $\mathbf{k}\cdot\mathbf{p}$ expansion of the spectrum (1) in powers of k_z.

In accord with the symmetry of the Brillouin zone, the total contribution of the states in the vicinities of the points of the Σ type to the perpendicular component of the susceptibility tensor can be written in the form

$$\chi_\perp^z=3(\chi_x^z+\chi_y^z). \tag{12}$$

The susecptibility at finite temperature can be calculated from the formula[14]

$$\chi(\mu,T)=-\int_{-\infty}^{\infty}dE\,\chi(E,0)\frac{\partial f(E-\mu)}{\partial E}, \tag{13}$$

where $f(E-\mu)$ is the Fermi-Dirac distribution function. To take into account the temperature dependence of the spectrum itself, the susceptibility $\chi(E, 0)$ must contain the spectrum parameters corresponding to the temperature T.

The results of the calculation of $\chi_\perp(\mu)$ for a number of temperature using (10)–(13) and the data of Fig. 3 are shown in Fig. 4. As the natural spectrum cutoff parameter k_Σ we chose half the neck of the hole "coronet." We note that these results differ quantitatively from those shown in Fig. 3 of Ref. 1, where the temperature dependences of the parameters of the spectrum (1) were not taken into account, only estimates were used for Q and L, and the value of k used there is actually half that indicated in the text and assumed in the present paper.

V. DISCUSSION OF RESULTS

From a comparison of the calculated $\chi_\perp(\mu)$ dependences at various temperatures (Fig. 4) with the experimental curve (Fig. 1) we can determine the behavior of $\mu(T)$. Two unknown factors participate in this comparison: the so-called background susceptibility, and the somewhat arbitrary cutoff parameter k_Σ. The background susceptibility is made up of all the contributions to $\chi_\perp$ not accounted for by expression (12), viz., the orbital susceptibility of the remaining states, the ionic diamagnetism, and the spin paramagnetism. It follows from the preceding[1] and present studies that only the last contribution can depend on temperature. However the component $\chi_\parallel$, as seen from Fig. 1, does not change in the interval 50–1500 K, and since the orbital contribution to $\chi_\parallel$ should not depend noticeably on the temperature,[1] the spin susceptibility

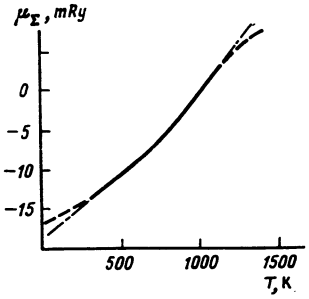

FIG. 5. Local position of the level of the chemical potential μ_ϵ vs. temperature. Solid curve—result of self-consistent calculation. The dashed sections of the curve correspond to k_Σ = 0.438 (a.u.)$^{-1}$, and the dash-dot ones to k_Σ = 0.4 (a.u.)$^{-1}$.

is also constant (a fortuitous cancellation of the temperature dependences of these contributions in so wide a temperature range is unlikely). Thus, the data of Figs. 1 and 4 differ by a background of constant magnitude, which can be determined and excluded when these data are reconciled. In first-order approximation the background is the difference between the extremal values on the experimental $\chi_\perp(T)$ curve at $T = 870$ K (Fig. 1) and on the calculated $\chi(\mu_\Sigma, T = 870\ \text{K})$ curve. Next, taking the background into account, we can find for each temperature the corresponding position of the chemical-potential level at which there is realized on the calculated curve a value of $\chi_\perp$ that agrees with the experimental one, i.e., obtain the approximate $\mu_\Sigma(T)$ plot. Rectification in the region $T \sim 870$ K yields a new value of the chemical-potential level for the extremum of the susceptibility $\mu_\Sigma(T = 870\ \text{K})$ and a new value of the background. When the graphical reconciliation procedure is repeated, the $\mu_\Sigma(T)$ lines converge rapidly to the plot shown in Fig. 5.

As to the leeway in the choice of the parameter k_Σ, variation of k_Σ within reasonable limits (0.3 – 0.438 a.u.) affects the $\mu_\Sigma(T)$ curve only at low (< 400 K) and very high (> 1300 K) temperatures (Fig. 5), i.e., beyond the possible limits of the validity of formulas (10) and (11). Thus, at low temperatures the chemical-potential level is relatively far from the critical point of the spectrum, and the $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian in the form (1) is no longer sufficient for the description of the investigated hole states. This explains the differences between the result $\mu_\Sigma(T = 4.2\ \text{K}) \approx -12$ mRy of Ref. 7, from that shown in Fig. 5. At very high temperatures the energy interval for the averaging of the susceptibility [see (13)] is also beyond the range of validity of the Hamiltonian (1).

The results for intermediate temperatures, which are stable to the variations of the parameter k_Σ, seem quite reliable (although we know of no other methods of obtaining or verifying analogous information), and can be used in the analysis of the general restructuring of the spectrum with changing temperature, a restructuring that causes the change of the chemical-potential level. As seen from Fig. 5, with increasing temperature the chemical-potential level approaches the band-degeneracy point, and passes through it at $T \approx 1050$ K.

We can thus draw the following conclusion on the basis of the experimental and theoretical results obtained in the present paper:

1. We have experimentally verified the existence of the anomaly, predicted in Ref. 1, of the diamagnetism $\chi_\perp$, and due to the band degeneracy in beryllium.

2. It was established that the observed singularity in the behavior of $\chi_\perp(T)$ can be described quantitatively only if account is taken of the temperature-induced changes of the spectrum parameters.

3. Comparison of the experimental $\chi_\perp(T)$ data with calculation yielded the dependence of the local value of the chemical-potential level μ_Σ on the temperature in the interval 400–1300 K.

4. From the constancy of $\chi_\parallel$ and the calculation of Ref. 1 it follows that there are no noticeable changes of the spin susceptibility at temperatures 50–1500 K.

[1]G. E. Grechnev and I. V. Svechkarev, Fiz. Nizk. Temp. 3, 770 (1977) [Sov. J. Low Temp. Phys. 3, 374 (1977)].
[2]B. I. Verkin, I. V. Svechkarev, and L. B. Kuz'micheva, Zh. Eksp. Teor. Fiz 50, 1438 (1966) [Sov. Phys. JETP 23, 954 (1966)].
[3]I. V. Svechkarev, Prib. Tekh. Eksp. No. 4, 142 (1963); R. B. Lyubovskiĭ and I. F. Shchegolev. Prib. Tekh. Eksp. No. 5, 234 (1968).
[4]A. Martin and A. Moore, J. Less-Common Metals 1, 85 (1959).
[5]G. P. Motulevich, Zh. Eksp. Teor. Fiz. 51, 1918 (1966) [Sov. Phys. JETP 24, 1287 (1967)].
[6]R. V. Kasovski, Phys. Rev. 187, 885 (1969).
[7]J. H. Tripp, P. M. Everett, W. L. Gordon, and R. W. Strak, Phys. Rev. 180, 669 (1969).
[8]M. Taut, Phys. Status Solidi B 54, 149 (1972).
[9]P. O. Nilsson, G. Arbman, and T. Gustafsson, J. Phys. F 4, 1937 (1974).
[10]F. Herman and S. Skillman, Atomic structure calculations, Prentice Hall, 1963, Chap. 6.
[11]R. W. Meyerhoff and J. P. Smith, J. Appl. Phys. 33, 219 (1962).
[12]R. Stedman, Z. Amilius, R. Pauli, and O. Sundin, J. Phys. F 6, 157 (1976).
[13]H. Fukuyama, Prog. Theor. Phys. 45, 704 (1971).
[14]F. A. Buot and J. W. McClure, Phys. Rev. B 6, 4525 (1972).

Translated by J. G. Adashko