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Interpretation of the de Haas–van Alphen experiments in MgB_2

I. I. Mazin*
Code 6391, Naval Research Laboratory, Washington, DC 20375-5000

Jens Kortus†
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany
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Recent reports on quantum oscillations in MgB_2 provide valuable information on three important aspects of this material: (i) electronic structure near the Fermi level, (ii) disparity of the electron-phonon interaction between the two systems of bands, and (iii) renormalization of spin susceptibility. However, extraction of most of this information requires highly accurate band-structure calculations of the relevant quantities. In this paper we provide such calculations and use them to analyze the experimental data.

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MgB_2, a superconductor with $T_c \approx 40$ K, has attracted enormous attention in the last year. The most popular model, suggested by Liu *et al.*[1] and Shulga *et al.*,[2] and elaborated upon by Choi *et al.*,[3] is the two-gap model, which, based on the very large interband disparity of the electron-phonon interaction (first noted in Ref. 4), predicts two different gaps for the two different band systems. The calculations[1,3] yield an effective (including an enhancement due to gap variation) electron-phonon coupling constant of the order of 1. On the other hand, the two-gap theory has a serious conceptual problem: Two distinctive gaps may exist only if the interband impurity scattering is very weak. That seems to be in contrast to the experimental observation that even poor quality, high-resistivity samples have very good superconducting properties. It has been argued[5,6] that the specificity of the electronic and crystal structures of MgB_2 results in a peculiar relation among the three relevant relaxation rates, namely that the impurity scattering inside the so-called π band is much stronger than inside the σ band, and the latter, in turn, is much stronger than the interband scattering. However, there has been no direct experimental confirmation of this claim.

On the other hand, some authors[7] argue that the calculated band structure is strongly renormalized by electron-electron interactions not accounted for in the local-density calculations, so that the plasma frequency is a factor of 5 smaller than the calculated one. This would imply an electron-phonon coupling constant less than 0.2. There are claims that infrared spectroscopy supports this point of view,[8,9] although other researchers in the field[5] dispute the interpretation accepted in Refs. 8 and 9. In any case, the fact that all optical experiments until now have been performed on polycrystalline samples undermines their value as a decisive test for the electronic structure calculations.

Single-crystal angular-resolved photoemission spectroscopy[10] (ARPES) measurements agree very well with the calculations.[11] However, some calculated bands were not observed, and, furthermore, ARPES probes only a very thin surface layer and is therefore often not representative of the bulk electronic structure.

Historically, the most reliable probe of the bulk electronic structure has been the de Haas–van Alphen effect (dHvA). Recent observation of this effect in MgB_2 single crystals[12] provides key information to assess the validity of the standard band-structure calculation. Given the fact that most theoretical papers rely on this band structure, the importance of a proper analysis of these data can hardly be overestimated. It must be emphasized that such an analysis requires highly accurate band-structure calculations, i.e., the use of a much finer k-point mesh in the Brillouin zone and a much more accurate integration than is customary in other applications of the band theory. In this paper we present such calculations and show that both Fermiology and effective masses (and hence the Fermi velocities and plasma frequencies) produced by conventional band-structure calculations are in excellent agreement with the experiment, thus giving a strong foundation for the widespread use of this band structure. Furthermore, we show that the calculational predictions of a strong disparity of the electron-phonon interaction in the two-band systems in MgB_2 are supported by the de Haas–van Alphen experiment, and that the scattering rates inside the σ band and between σ and π bands are probably much smaller than inside the π bands.

The Fermi surface of MgB_2 consists of four sheets.[13] Two sheets come primarily from the boron p_x and p_y states, and form slightly (nearly sinusoidally) warped cylinders, σ (bonding) and σ^* (antibonding),[14] and two tubular networks, the bonding one, π, in the Γ ($k_z=0$) plane, and the antibonding one, π^*, in the A ($k_z=\pi/c$) plane. There are six extremal cross sections for the field parallel to k_z (along the ΓA line). These are (1) σ in the Γ plane, (2) σ^* in the Γ plane, (3) π in the Γ plane (''holes'' between the tubes), (4) σ in the A plane, (5) σ^* in the A plane, and (6) π^* in the Γ plane. For a field parallel to k_y (perpendicular to the ΓAM plane) there are two extremal cross sections (tubes' necks), for the π surface (7) and for the π^* surface (8).

We performed highly accurate and well-converged full potential linear augmented plane-wave (LAPW) calculations, using the WIEN-97 package,[15] including local orbitals[16] to relax the linearization errors. We used the generalized gradient approximation of Perdew-Wang[17] for the exchange-correlation potential. By comparing the results with linear muffin-tin orbitals calculations, we found that for a proper description of the σ orbits it is essential to use a full potential method. It is furthermore essential to use a very fine mesh in

TABLE I. Calculated de Haas–van Alphen parameters from present work (F_{calc}) compared to the experimental data (F_{exp}) of Ref. 12. The masses are given in free-electron mass units.

	Orbit	F_{calc} (T)	m^{calc}	dm^{calc}/dE (Ry^{-1})	λ^{a}	$\lvert(1+\lambda)m\rvert^{b}$	F_{exp} (T)	$\lvert(1+\lambda)m\rvert^{\mathrm{exp}}$
(1)	σ Γ plane	730	−0.251	1.1	1.25	0.56	540	0.54
(2)	σ^* Γ plane	1589	−0.543	2.7	1.16	1.17		
(3)	π Γ plane	34630	1.96	23	0.43	2.80		
(4)	σ A plane	1756	−0.312	1.2	1.25	0.70	1530	0.66
(5)	σ^* A plane	3393	−0.618	2.3	1.16	1.33		
(6)	π^* Γ plane	31130	−1.00	4.1	0.47	1.47		
(7)	π ΓAM plane	458	−0.246	1.5	0.43	0.35		
(8)	π^* ΓAM plane	2889	0.315	0.8	0.47	0.46	2685	0.45

[a]Computed from Tables 1 and 2 of Ref. 1.
[b]Computed from the preceding columns.

k space; we employed a 38×38×27 mesh, corresponding to 1995 inequivalent **k** points. To achieve sufficient accuracy for the small areas of the orbits 1, 2, 4, 5, 7, and 8, we used an integration engine built in the SURFER program,[18] which internally interpolates the integrand with splines.

The bare (band) masses in the third column of Table I were then calculated by varying the Fermi energy and using the standard formula,

$$m_{\mathrm{dHvA}}=\frac{\hbar^2}{2\pi}\frac{dA}{dE}. \tag{1}$$

Here and below we use the notation A for the areas of the orbits in standard units and F for those in Tesla units. In order to obtain the energy derivatives we fitted the calculated $A(E)$ by quadratic polynomials in the ranges of about 0.03 Ry around the Fermi energy. The experimentally observed ''thermal masses'' differ from the ''band'' masses by a renormalization factor of $(1+\lambda)$, where λ is the coupling constant for the interaction of electrons with phonons or other low-energy excitations. For Table I we used the values of λ computed in the following way (see, e.g., Ref. 19): we assumed that the matrix elements of the electron-phonon interaction are constant within each of the four bands (a good approximation, see Ref. 3), but different among the bands and for different interband transitions. If the matrix of the electron-phonon interaction is U_{ij}, where i,j are the band indices, then the mass renormalization in the band i is

$$\lambda_i=\sum_j U_{ij}N_j, \tag{2}$$

where N_j is the partial density of states per spin for the ith band. Recall that the conventional Eliashberg coupling constant is $\lambda=\Sigma_{ij}U_{ij}N_iN_j/\Sigma_iN_i$. The matrix U and the vector N calculated in Ref. 1 were used to compute the fifth column in Table I.

The agreement between the calculated and measured thermal masses can be characterized as excellent. Very importantly, *this agreement is so good only because the calculated electron-phonon coupling differs by a factor of 3 between the σ and π bands*. This is a direct demonstration of this important effect. The agreement between the calculated areas F and the experiment is also very good. Although F_1, F_2, and F_3 are overestimated by 35%, 15%, and 8%, respectively, the absolute values of these errors are only 0.5% (or less) of the total area of the corresponding Brillouin-zone cross sections. Even better appreciation of the significance of these errors can be gained from the observation that shifting the σ band by 6.3 mRy down, and the π^* band by 5.5 mRy up brings the calculated areas to full agreement with the experiment. It is not at all clear whether or not such a small discrepancy with the experiment is meaningful. It is interesting, nevertheless, that after such an adjustment of the band positions the calculated masses agree with the experiment even better: for the three orbits in question the electron-phonon coupling constants deduced from the experiment by taking the ratio of the measured masses to the calculated masses are, respectively, 1.15, 1.12, and 0.43. After the Fermi-level adjustment, they are 1.22, 1.18, and 0.45. It is also worth noting that, for instance, a change in the c/a ratio of 1.5% shifts the σ and π bands with respect to each other by ≈12 mRy, or that a shift of the Fermi level by 6 mRy corresponds to a 0.05 e change in the number of electrons. This shows how sensitive the de Haas–van Alphen results are to the crystallography and stoichiometry.

Another important observation reported in Ref. 12 is the so-called ''spin zero.'' This is a suppression of the de Haas–van Alphen amplitude when the difference in the areas (in Tesla units) of the spin-split (by the external field H) cross sections is exactly $H/2$. This effect has been observed for orbit (8) in the field $H=17$ T, when the field was tilted with respect to the crystallographic axis by $\phi=15-18°$. This means that $(F_8^{\uparrow}-F_8^{\downarrow})/\cos(\phi)=8.5$ T, or $\Delta F_8=F_8^{\uparrow}-F_8^{\downarrow}\approx 8.1$ T (note that the angle itself does not depend on the field in which the measurements are performed, but only on the Fermi-surface geometry and Stoner renormalization). It is easy to estimate this splitting in the first approximation, using the data from Table I and the Stoner renormalization of 33%, calculated in Ref. 21: $\Delta A_8=2\pi m\Delta E_{xc}$, where $\Delta E_{xc}=2\mu_B H(1+S)$ is the induced spin splitting of the bands near the Fermi level, enhanced by a Stoner factor $(1+S)$. This formula gives $\Delta F_8\approx 7.1$ T. A caveat here is that the induced spin splitting need not be the same for all bands, in other words, while the *average* S is 0.33, individual S's may

vary from orbit to orbit. To avoid this problem, we performed self-consistent LAPW calculations in an external field of 1.8 kT (still well within the linear-response regime) and measured $d\Delta A_8/dH$ explicitly. Using these results, we found that for the actual field of 17 T, $\Delta F_8 = 6.7$ T, close to, but slightly smaller than the above estimate of 7.1 T. In other words, the calculated Stoner factor for this orbit is $S_8 = 0.26$, smaller than the average over all bands, which is 0.33. Note that the experimental number of 8.1 T can be reconciled with the calculated mass, if S_8 were ≈ 0.5, fairly close to the electron-phonon coupling constant for the same band, 0.47. We, however, believe that the coincidence is accidental, although we do not have any plausible explanation for the noticeable underestimation of the Stoner factor for this orbit. No ''spin-zero'' effect has been observed for the orbit (4), which has essentially the same mass as orbit (8). Our calculations for this orbit give $\Delta F_4 = 6.9$ T; that is, the calculated Stoner factor for this orbit is $S_4 = 0.31$. At the same time, the actual Stoner factor must be either larger than 0.60 or smaller than 0.18, for this orbit not to exhibit the ''spin-zero'' effect [this is neglecting deviations from a cylindrical shape, which are noticeably stronger expressed for this orbit than for the orbit (8)]. Further experimental studies on better samples should give more insight into this problem.

Finally, we would like to discuss the problem of the ''missing orbits.'' The amplitude of the de Haas–van Alphen signal is proportional to[22]

$$H^{-1/2}\frac{X}{\sinh X}\exp\frac{-c\hbar\sqrt{\pi A}}{eHl}\cos\frac{\pi\Delta F}{H}X = \pi^2 mc(1+\lambda)k_B T/\hbar eH,$$

where l is the mean free path for the orbit in question. Thus, it is not surprising that the large orbits (3) and (6) are not observed; the Dingle exponent $c\hbar\sqrt{\pi A}/eHl$ is at least ten times larger than for the other orbits. However, the question remains for the orbits (2), (5), and (7). Let us start with the first two. We observe that, compared to the orbits (1) and (3), both the Dingle factor and the thermal factor are reduced. The latter is smaller because the effective mass $m(1+\lambda)$ is twice larger, which reduces the maximal temperature at which these orbits can be observed by a factor of 2. The former is reduced because both the orbit size, $\sqrt{A}$, is larger, and the mean free path, $l \propto v_F$, (assuming the relaxation time is the same for both σ and σ^* bands), is smaller [from Table 1 of Ref. 21, $v_F(\sigma)/v_F(\sigma^*) \approx 1.4$]. The total reduction of the Dingle exponent compared to orbit (4) is by a factor of 2 for orbit (5), and of 1.4 for orbit (2).

The absence of a signal from the orbit (7) seems puzzling. Its area and its thermal mass are the smallest of all orbits, and the average velocity for this band is the highest (50% higher than for the σ band). A very plausible explanation is that, as conjectured in Ref. 5 and elaborated upon in Ref. 6, the impurity scattering rates differ drastically between the bands. If the dominant defects reside in the Mg plane (e.g., Mg vacancies), then such defects are very weak scatterers for the σ bands for the simple reason that those bands have very little weight at the Mg atoms. However, this simple picture does not explain why orbit (8), originating from the π^* band, apparently has a small relaxation time and therefore is seen in experiment. Its velocity is close to (in fact, 15% smaller than) that of the π band and its linear size is more than twice larger than that of orbit (7), so the scattering rate has to be at least five times larger. We do not have a plausible answer as to why the impurity scattering appears to be so suppressed for this orbit. Possibly, this is related to its parity (while the π band is even with respect to the $z \rightarrow -z$ reflection, the π^* band is odd).

To conclude, we presented highly accurate calculations of the de Haas–van Alphen parameters for MgB_2. Comparison with the experiment reveals (i) absence of any mass (velocity) renormalization apart from that due to phonons; (ii) a good agreement of the calculated cross-section areas with the experiment; (iii) excellent agreement of the calculated electron-phonon coupling with the dHvA mass renormalization, including very large disparity between the coupling of the σ and π bands, which clearly confirms the basic assumption of the two-gap model for superconductivity in MgB_2; (iv) some underestimation, despite a good qualitative agreement, of the calculated and measured Stoner factors for the π bands, (v) indirect evidence of substantially different impurity scattering rates in the σ and π bands, and (vi) a problem that remains to be understood, the total suppression of the neck orbit, associated with the bonding π band, given a clear observation of the much larger orbit from the electronically similar π^* band.

After this work was finished, we learned about similar works by Rosner *et al.*[20] and Harima.[23] Their results, particularly those of Ref. 20, are quite close to ours. Both papers employ similar methods and take full care of the k-mesh convergence. The remaining difference is a good gauge of how reliable such calculations are, in a technical sense.

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*Electronic address: mazin@dave.nrl.navy.mil

†Electronic address: j.kortus@fkf.mpg.de

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