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JARLBORG, Thomas N.


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Importance of thermal disorder and electronic occupation for temperature dependence of optical conductivity in FeSi and MnSi

T. Jarlborg

DPMC, University of Geneva, 24 Quai Ernest-Ansermet, CH-1211 Geneva 4, Switzerland

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The spectral weight (SW) for optical transitions in FeSi and MnSi are calculated as a function of temperature by means of linear muffin-tin orbital–local density approximation band calculations. The main effects, caused by structural disorder and electronic Fermi-Dirac distribution, act oppositely on the T dependence of the SW, while the variation of the magnetic moment in MnSi has only a minor effect. The calculations agree with the experimental findings of an increasing SW in FeSi and a decreasing SW in MnSi as function of T. The results can be understood from the change of the band structure with disorder.

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I. INTRODUCTION

Binary compounds of the B20 structure, such as MnSi, FeSi, and FeGe, exhibit many unusual properties. FeSi is known for the uncommon crossover from being a narrow-gap semiconductor at low T to an exchange enhanced paramagnetic metal at room temperature.1 Band calculations agree on the fact that there is a small gap of the order 6 mRy at low T,2,3 and this is also close to the experimental value.1 Different mechanisms, such as strong correlation,4 Kondo screening,5,6 and thermal disorder,7,8 have been proposed for a description of the high-T behavior. The iso-electronic FeGe is ferromagnetic (FM), but with a strong pressure (P) dependence and a possible suppression of FM at high P.9 MnSi has 1 electron less/f.u., and it is FM with helical spin order.10 Many questions about the magnetic state in MnSi are still unresolved, as is reflected by many inconsistencies between spectral data, magnetic moment, and band calculations.11,12 The experimental moment for MnSi, about 0.4μB/f.u., is a factor of 2 smaller than what is found from band calculations (which do not search for the possibility of helical spin order) at the calculated equilibrium lattice constant.13,14

Recent studies of MnSi with the technique of x-ray absorption suggest a correlated excite state, and the interpretation in terms of band structure is complicated by the involvement of a core hole.12 However, through high-resolution optical measurements, it has been possible to detect T-dependent details of the band structure in several B20 compounds.15–20 The band filling of the small gap in FeSi as a function of raising T has been observed, but with an unexplained missing intensity of the total spectral weight (SW) (the integrated optical conductivity) at least for energies up to a few eV. This has been taken as an indication of exotic, Kondo-like, and band-unlike interactions in FeSi.15 Subsequent measurements concluded that the weight is essentially conserved for energies below −0.4 eV.16 Complementary optical measurements in other B20 compounds show that the nonconservation of the spectral weight is quite general, and with contrasting behavior in FeSi and MnSi.17 From the view of local density approximation (LDA) bands, it is not evident that the SW should change with temperature. Previous band calculations, where a disordered supercell is modeling the effect of thermal disorder, explain the band filling, transport properties, and other observed T dependencies in FeSi.7,8 However, the question about nonconservation of the SW was not addressed.

Here, we present band results and simulation of optical conductivity, σ(E, T), in FeSi and MnSi with emphasis on two temperature dependent mechanisms. One is coming from thermal disorder of the lattice and the other from electronic temperature coming from the Fermi-Dirac (FD) occupation. The effect of magnetism is verified by comparing FM and nonmagnetic solutions. The investigations are done through linear muffin-tin orbital21,22 band calculations in the LDA (Ref. 23) for ordered and disordered 64-atom supercells (2×2×2 extension of the elementary cell) as has been described previously.8

II. METHODS OF CALCULATION

Thermal disorder is a result of lattice vibrations. The phonon frequencies Ω(k) do not depend much on T for harmonic vibrations, but the vibrational amplitudes u do. The relation between vibrational amplitudes and T is known.24 The vibrations are essentially harmonic and almost all phonon modes are occupied when T is comparable to the Debye temperature. It is then a good approximation to consider the vibrations of atomic neighbors as uncorrelated. Structural disorder can in this case be described by a Gaussian distribution function, g(u), where δ is the mean-square average of all atomic displacements u.24

\[ g(u) = \left(\frac{1}{2\pi\delta^2}\right)^{3/2} e^{-u^2/2\delta^2}. \]

Furthermore, the average \(\langle u^2 \rangle\) (i.e., \(\delta^2\)) is related to the temperature and the force constant \(K=M\Omega^2\), where \(M\) is the atomic mass and \(\Omega\) is the characteristic phonon frequency. At high T,

\[ \langle u^2 \rangle = 3k_BT/K. \]

The time scale of vibrations is long in comparison with the time scale of electrons (because of the large ratio between atomic and electronic masses), and the electronic structure can be solved for a “static” lattice according to the Born-Oppenheimer approximation. We are interested in the
optical properties at a few hundred kelvins, which is in the range of harmonic approximations. The deviation of the atomic positions from the equilibrium is given by \( u_{ij} \), where \( i=x,y,z \) and \( j \) is the index for the atom, leading to \( 3 \times 64 = 192 \) degrees of freedom in the unit cell. The values of all \( u_{ij} \) are obtained by a random number generator, but a rescaling is done so that the distribution of all 192 numbers follow the function \( g(u) \). It is also required that the \( \delta \) of each distribution corresponds to the correct temperature according to Eq. (2). A sufficiently large number of static configurations are needed for convergence, either as a large supercell or as a sum of smaller configurations. Different configurations (with the same \( \delta \)) within a 64 atom supercell of FeSi was found to give similar density-of-states (DOS) features, and we chose one configuration of the same type of cells here.

An additional approximation is to assume that the displacements of Fe (or Mn) sites are of the same amplitude as of Si sites. However, the atomic masses are too different and \( \langle u_{ij}^2 \rangle \) and \( \langle u_{ji}^2 \rangle \) are comparable. Moreover, the electronic structure is such that Si displacements are of minor importance, since the dominant \( d \)-DOS comes from the transition metal.

Zero-point motion (ZPM) (where \( \delta^2 = 3\hbar \Omega/2K \)) is not considered in this work, although small effects of ZPM might be present in FeGe. The small gap in FeSi (6 mRy) is too large to be closed by the ZPM at low \( T \), but in FeGe at large \( P \), where the corresponding gap is close to zero, ZPM might be important. Omission of ZPM implies that by comparing SW from ordered and disordered structures, one may slightly exaggerate effects of thermal disorder. Effects of electron-phonon coupling or spin fluctuations could be of importance in systems with large DOS at the Fermi energy (\( E_F \)). Such effects, as well as effects of thermal expansion, are ignored in this work.

Dynamical effects due to excitations of lattice vibrations are different from what are studied here. Vibrational modes can be excited, which is seen as sharp peaks in the infrared energy range of absorption spectra. Except for some broadening, it is not expected that the resonance frequencies for vibrational excitations should change much with \( T \). However, the effect from vibrational disorder on the electronic band structure is always present. A certain disorder is in thermodynamical equilibrium at some \( T \), and abiatatic heating (or cooling) makes the degree of disorder different.

The self-consistent convergence is relatively slow for the large supercells and the calculations are restricted to two supercell configurations, both containing 64 atoms. One cell is perfectly ordered (low \( T \)) and the other is disordered (high \( T \)) with a mean displacement \( \delta \) of the atomic positions of 0.019a₀, where \( a₀ \) is the lattice constant. This corresponds roughly to a temperature of 500 K according to the measured data in Ref. 25 and is slightly higher to what was estimated in Ref. 8. By comparison, the ZPM from the same data corresponds to displacements of about 0.006a₀. Instead of searching for a continous \( T \) variation of the SW, we present the trends and reasons for nonconserved SW in the different B20 compounds by comparing the low-\( T \) and high-\( T \) results. The final bands are calculated with equivalent density of \( k \) points for the ordered and disordered structures, for 125 \( k \) points within 1/8 of the Brillouin zone for the former case and 405 points with half of the zone for the latter case. All sites are considered as nonequivalent, i.e., all sites can have different potentials, charges or magnetic moments throughout the calculations. Other details of the calculations are described in Ref. 8.

The optical conductivity \( \sigma(E) \) is related to the imaginary part of the dielectric constant,

\[
\sigma(E) \sim \sum_{i,j,k} \frac{f(e_i^j) - f(e_j^k)}{e_j^k - e_i^j} \delta(e_j^k - e_i^j - E) M^2. \tag{3}
\]

The evaluation of this expression contains a summation of band energies, \( e \) (\( i \) occupied and \( j \) unoccupied), and \( k \) points (\( k \)). For MnSi, there is also a summation over the two spins. The matrix element \( M \) is calculated in the dipole approximation

\[
M = \sum_{q} \int_{0}^{\infty} \Psi_{q,\ell,m}(e_j^k, r) \tilde{\rho} \Psi_{q,\ell',m'}(e_j^k, r) d^3r, \tag{4}
\]

where \( \Psi \) are the wave function for the corresponding band and \( k \), which includes \( s, p \) and \( d \) states, and \( \tilde{\rho} \) is the muffin-tin radius for site \( q \). The angular part of \( M \) leads to the dipole selection rule. Only transitions where \( \ell - \ell' = \pm 1 \) and \( m - m' = \pm 1,0 \) are allowed, and the radial part can be simplified further.\(^{27}\) The SW is here defined as the energy integral of \( \sigma(E) \).

The self-consistent band calculations are made including a FD broadening of 1.3 mRy (~200 K). It is conceivable that a different FD occupation, corresponding to a different \( T \), would lead to a change in band structure, which suggests that \( T \)-dependent bands \( \epsilon_i^j(T) \) should be used in Eq. (3). However, test calculations show that the \( T \) dependence of the band structure via the FD occupation is very small. This is probably because of the dominant Fe \( d \) character of the bands near \( E_F \), so that even if there is a wider occupation of states across \( E_F \) at a higher \( T \), it will always involve the same type of states (Fe \( d \)), and the charges and the self-consistent solutions remain \( T \) independent. Hence, for the studies of \( \sigma \) as a function of FD occupation, it is a reasonable approximation to evaluate Eq. (3) as it is written, i.e., the FD factor \( f \) occupies states within “fixed” bands, \( \epsilon_i^j \). This implies also that the ambition is not to go beyond the Koopmans theorem in the calculations of the transition probabilities.

III. RESULTS AND DISCUSSION

This method was applied recently to FM FeGe, and the sequence and the relative intensities of \( \sigma(E) \) agree favorably with experiment, however, with two important differencies. First, the energy scale needs to be shifted by several tenths of an eV. Secondly, the experimental spectrum is far less structured than the calculated one. The latter can be attributed to lifetime broadening, which is not included in the calculation. Similar deviations can be expected for MnSi, FeSi, and CoSi.\(^{19}\) Therefore, we do not aim at a detailed comparison with experimental data, but we concentrate on the relative
difference in two calculations of $\sigma(E, T)$, where the computational procedures are identical except for difference in temperature.

A few mechanisms can be imagined to cause nonconservation of the SW. Any $T$-dependent variations of the FM moment in MnSi, which remove or add spin states near $E_F$, could change the allowed transitions across $E_F$. This effect is small, since the amplitude of local FM moments is found to be rather stable. The $T$ dependence of the FD occupation is well controlled in the band approach. If the DOS at $E_F$ is large (as in the FM compounds MnSi and FeGe), it can reduce a considerable part of the SW within an energy range of $k_BT$. The effect on the dipole matrix element from disorder is more subtle. A closer look at the $\ell$ character of the bands in ordered and disordered structures reveals a small transfer of $d$ states toward other $\ell$ states, when the structural disorder is important, as is shown in Table I. (An increase of $f$ character is found in calculations with disorder within an elementary eight-atom cell.) Thus, dipole transitions are stronger for increasing $T$. This remark concerns these B20 compounds because of their exceptionally large Fe $d$ (or Mn $d$) character of the bands within a few eV around $E_F$. Disorder will also change the band structure. Simply speaking, this can be resumed into the effect of band broadening. A normal degenerate band will be multiply split when it is projected on the band structure of the disordered supercell. Interband transitions between the splitted bands are equivalent to Drude-like intraband transitions within the original band (across $E_F$), and the band broadening becomes larger for increasing disorder.

First, we present results for paramagnetic (PM) and FM MnSi, ordered and disordered. The calculation for ordered, FM MnSi gives a moment of about $0.63\mu_B$/f.u., which is lower than at the calculated equilibrium volume and larger than the experimental moment. However, as will be seen, the SW is quite insensitive to the magnetic moment. The moment is uniformly distributed on all (Mn) sites, when the structure is perfectly ordered. The average moment for structurally disordered MnSi decreases slightly, to $0.58\mu_B$/f.u., but with a very unequal distribution. The highest local Mn moment is about three times larger than on the Mn site with the lowest moment. Thus, structural disorder is accompanied by a large spin disorder.

The two spin DOS functions near $E_F$ differ more and more when the average moment exceeds $\sim0.6\mu_B$.$^{13}$ The DOS of PM MnSi is quite different from the two FM band structures, when the exchange splitting is reduced to zero from about 0.5 eV in the FM cases. The effect of magnetism on $\sigma$ for the FM, disordered case is masked by additional effects coming from disorder, as will be discussed later. Despite these differences in the three cases of MnSi there is a surprising similarity of the $\sigma$’s shown in Fig. 1 for a FD temperature of about 300 K. The general shape and the absolute levels are basically the same. It seems that the large number of Mn $d$ states near $E_F$ allow for many transitions and the differences in band structure are not sufficient for being seen in $\sigma$. It should be noted that the PM and FM calculations describe very different electronic structures, much more different than what can be expected to be the case for MnSi, when $T$ increases from 0 to 300 K. The conclusion is that $T$ variations of FM is not the cause for the increasing SW in MnSi.

Figure 2 shows that the $T$-dependent FD occupation has large effects for $E=h\omega$ below $\sim1$ eV. Such an effect is stronger in a material with large $N(E_F)$, as in MnSi. The

important transitions start at higher energies in FeSi and CoSi because of their deep DOS minimum near $E_F$ (see Fig. 3), and the effect of the FD occupation is smaller. The $E$ sum of $\sigma(E,T)$, the SW, evaluated at high $T$ remains below the low-$T$ curve, also at large $E$, because of the loss of transitions at low $E$. This mechanism explains the reduction of the SW for increasing $T$ as is observed in MnSi (Ref. 17) and in FeGe above $\sim 0.1$ eV.20 The same reason of transition probabilities explains why the SW curve for a high-DOS material (MnSi, FeGe, etc.) is above that for a low-DOS material (FeSi, CoSi, etc.).

The effects of disorder on $\sigma$ is twofold in the case of FeSi. First, the band structure itself will change because of the structural disorder, so that the small gap of about 6 mRy at low $T$ will be closed at intermediate $T$ and completely filled at large $T$ (see Fig. 2 in Ref. 8). This fact will not change the total SW. It will just “broaden” the band states and redistribute $\sigma$ to other, not very different energies $h\omega$. Secondly, there are effects on the matrix elements. Figure 4 shows $\sigma(\omega)$ for ordered and disordered FeSi for equal $T$ of the FD distribution. The first effect, the filling of the gap, is seen below $\sim 1000$ cm$^{-1}$ (1/8th of an eV), but the curve for disordered FeSi (high $T$) seems to be above the low-$T$ curve even for quite large energies. The same observation can be made for MnSi in Fig. 1. As was discussed above, the reason is that the dipole approximation allows for increased transition probabilities at large disorder, because of the general trend of promoting $d$ states into $p$ or $f$ states. The band structures are similar for all these 3d transition metal compounds of B20 structure, and the calculated effects on the SW in PM FeSi and FM MnSi are about equal.

The effect of structural disorder on the matrix elements is the only mechanism which is found to increase the SW for increasing $T$. If MnSi is FM or not has only a minor effect on the SW, and even fluctuations of the spin amplitude on each site turns out to be unimportant. The effect of strong correlation is not investigated, and if it can be shown that correlation is important for the properties of these materials, it could also affect the optical properties. It can be recalled, however, that the effect of thermal disorder on the electronic structure of FeSi explains many of the unusual key properties of this material.8 It is therefore likely that a $T$ dependence of the SW will come from thermal disorder and FD occupation.

The final result depends on the strength of the different mechanisms. The calculated SWs at low $T$ (ordered structure and $T \sim 80$ K in the FD occupation) and high $T$ (disordered structure with $T \sim 500$ K in the FD occupation) for FM MnSi and (PM) FeSi are shown in Fig. 5. The temperature of the lattice (structural disorder) and of the electrons (FD occupation) are chosen to be equal. It is seen that the effect from the FD occupation is dominating in MnSi, since the SW decreases at high $T$. The opposite behavior is seen for FeSi. First, the low-$T$ SW is zero below $\sim 0.1$ eV, and the high-$T$ curve is nonzero because of the absence of the gap. However, the high-$T$ curve is above the low-$T$ curve for FeSi also at higher energies, mainly because of matrix-element effects. The opposite $T$ dependence in FeSi and MnSi agree with the experimental findings.17 It can be understood from the relatively low DOS near $E_F$ in FeSi, which makes the effect from FD occupation weaker than the effect from disorder. The lower DOS explains also why the SW curves for FeSi is below those of MnSi.

A. Comparison with CoSi and FeGe

The experimental SW in CoSi show almost no $T$ dependence.17 This nonmagnetic compound has one more electron per transition metal compared to FeSi, and $E_F$ falls
in a wide valley with very low DOS, but there is no gap (see Fig. 3). The valley is too wide to be filled by neighboring states for realistic disorder. The effect of increasing SW is smaller in CoSi than in FeSi, and it could lead to a cancellation of the two mechanisms, at least for energies smaller than the width of the valley.

The recently measured SW in FeGe shows a decrease below $\sim 0.1$ eV and an increase above this energy for increasing $T$.\(^{20}\) FeGe is isoelectronic with FeSi, but it is FM with a saturation moment of about $1\mu_B$/f.u. and with a high DOS of the minority states. Band calculations are consistent with this moment and its strong variation with pressure.\(^9\) The majority band structure is similar to the one of CoSi, with $E_F$ in a wide DOS valley, with only a moderate effect from the mechanism of FD occupation. The $T$ dependencies at low $E$ should therefore mostly be caused by the minority bands, which are quite similar to those of PM MnSi. The high minority DOS at $E_F$ makes the process of FD occupation efficient to cause a reduction of the SW at low $h\omega$, while the effect from matrix elements should dominate for large $E$ and make the SW larger as a function of $T$.

IV. CONCLUSION

It is shown that thermal effects from structural disorder and electronic excitations are important for an understanding of the observed trends for the $T$ dependence of the spectral weight in FeSi and MnSi. The two mechanisms work in general oppositely on the $T$ dependence. Details of the band structures of FeSi and MnSi, mainly the presence of a small gap in the former and a high DOS for the latter, makes one or the other effect dominant. It is somewhat surprising to find that PM or FM band structures in MnSi lead only to minor differences in $\sigma$, even when disorder of the moments are taken into account. These results lend further support to the idea that thermal disorder is the main cause for the unusual $T$-dependent properties of FeSi. The unique band feature of a very narrow gap at $E_F$ makes this compound special in many respects.

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