Coalescence of the Fermi-surface-related diffuse intensity peaks in disordered alloys

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The possibility of disappearance of the diffuse-intensity peak splitting induced by the Fermi surface (i.e., of coalescence of the intensity maxima) with decreasing temperature is predicted. The underlying mechanism is the compensation of the reciprocal-space curvatures of the self-energy and the interaction. The theory also describes similar results obtained earlier for two low-dimensional models with competing interactions. The coalescence is compared with the recently observed “thermal” splitting in Pt-V which can be explained in the same way.

In the recent paper (Tsatskis 1998a) we proposed an explanation of the temperature dependence of the diffuse-intensity peak splitting found for the disordered Cu₃Au alloy (Reichert, Moss and Liang 1996; see also Reichert, Tsatskis and Moss 1997). The splitting is associated with the Fermi surface (FS) effects and is observed also for other FCC alloy systems: Cu-Al (Scattergood, Moss and Bever 1970, Schönfeld et al. 1996), Cu-Pd (Ohshima and Watanabe 1973, Ohshima, Watanabe and Harada 1976, Saha, Koga and Ohshima 1992), Cu-Pt (Ohshima and Watanabe 1973, Saha and Ohshima 1993), etc. It is the consequence of the indirect interaction between alloy atoms via conduction electrons in those cases where the FS has flat or nested (i.e., identically curved) areas (e.g., Krivoglaz 1996). The resulting effective long-range pairwise interatomic interaction is characterized by minima at some positions between the $X = (110)$ and $W = (1\overline{1}0)$ special (Lifshitz) points (SPs); this feature is then reflected in the short-range order (SRO) diffuse intensity (Fig. 1). According to the proposed theory, the temperature-dependent splitting is the non-mean-field effect and the result of the wavevector dependence of the so-called self-energy. The self-energy $\Sigma$ of the pair correlation function (for detailed discussion and relation to thermodynamics, see Tsatskis 1998b) enters the expression for the SRO intensity,

$$I(k) = \frac{1}{c(1-c) \left[ -\Sigma(k) + 2\beta V(k) \right]} \quad (1)$$

where $k$ is the wavevector, $I(k)$ is the intensity in Laue units, $c$ is the concentration, $\beta = 1/T$, $T$ is the temperature in energy units and $V(k)$ is the Fourier transform of the pair ordering potential $V_{ij} = (V_{ij}^{AA} + V_{ij}^{BB})/2 - V_{ij}^{AB}$. Potential $V_{ij}^{AB}$ corresponds to the interaction between an atom of type $\alpha$ at site $i$ and an atom of type $\beta$ at site $j$.

The $k$-dependence of the self-energy leads to the temperature-dependent shift of the $I(k)$ peak with respect to the corresponding minimum of the interaction $V(k)$ and, as a result, to the temperature dependence of the splitting. The positions of the $I(k)$ extrema are determined by the condition $\partial_k I = 0$ which gives

$$2 \partial_k V = T \partial_k \Sigma \quad (2)$$

Here $k$ is the wavenumber along a line (e.g., $(h10)$ or $(1k0)$ in Fig. 1) containing off-SP peaks; in what follows only the $I(k)$ profile along this line is analysed. Eq. (2) shows that the $k$-dependent self-energy shifts the intensity peak position away from the $V(k)$ minimum. The right-hand side of Eq. (2) contains $T$ as a factor, and $\Sigma(k)$ itself is a function of $T$, while the left-hand side is $T$-independent. The shift and the splitting (which are linearly related) depend therefore on temperature. In the two widely used theories of SRO, the mean-field Krivoglaz-Clapp-Moss (KCM) approximation (Krivoglaz 1969, Clapp and Moss 1966, 1968) and the spherical model (SM) (e.g., Brout 1965), the self-energy is $k$-independent, the right-hand side of Eq. (2) vanishes, the $I(k)$ peaks coincide with the minima of $V(k)$, and the splitting does not change with temperature.

This treatment, however, implicitly assumes that in Eq. (1) the $k$-dependence of the interaction term $2\beta V(k)$ in the area of the splitting is dominant. In this case the profile of the intensity closely follows that of the interaction, and there exists one-to-one correspondence between the $V(k)$ minima and the $I(k)$ peaks. The $k$-dependence of the self-energy in this part of the reciprocal space is relatively weak, though qualitatively important for the description of the temperature-dependent splitting. Such assumption is certainly correct at sufficiently high temperatures, where the KCM approximation (in which the self-energy is $k$-independent) works reasonably well. Meanwhile, as temperature decreases, $\Sigma(k)$ grows faster than $2\beta V(k)$, since the first correction to the KCM self-energy is of order $(\beta V)^2$ (Tsatskis 1998a,b). We can then encounter a situation where the variations of $\Sigma(k)$ and $2\beta V(k)$ with the wavevector are comparable. With temperature decreasing further, the $k$-dependence of the self-energy may even become considerably stronger; the $I(k)$ peak positions would then be determined by the $\Sigma(k)$ maxima.
of the order parameter. The only difference here is that the role of temperature is reversed: the inverse intensity $I_T$ is positive. In the vicinity of the second-order coefficient $a$, we can assume that in the area of the splitting terms are needed; since a SP serves as the origin, the expansions do not contain odd powers of $k$. Eqs. (5) for $I(k)$ and $\Sigma(k)$ thus behave in almost the same way as the Landau free energy, and its variation with $\Sigma$ becomes more and more important in comparison with that of $2\beta V(k)$ as temperature decreases. Then the qualitative picture of the temperature behaviour of the splitting is as follows: At high temperatures $\Sigma(k)$ is almost $k$-independent, and the $I(k)$ peak positions deviate little from the minima of $V(k)$. As temperature decreases, the $k$-dependence of $\Sigma$ becomes more pronounced; the peaks move farther away from the $V(k)$ minima and towards that $SP k_0$ (either $X$ or $W$) at which $\Sigma(k)$ has a maximum. Eventually, as temperature reaches certain value $T_0$, the intensity peaks coalesce at this $SP$ and the splitting disappears (Fig. 2). This effect has never been observed experimentally, though Reichert et al. (1996) assumed that (i) the coalescence took place at the first-order transition temperature $T_i$ (denoted there by $T_0$) and (ii) the splitting grew with increasing temperature as $(T - T_i)^{s}$; the bifurcation exponent $s = 0.38 \pm 0.15$ was determined by fitting to experimental data. The coalescence temperature $T_0$ can be found from the condition of vanishing second derivative of $I(k)$ at the SP $k_0$, since its sign controls the presence or absence of the splitting. At the $SPs$ all the first derivatives vanish, and from Eq. (3) it follows that

$$\left(\partial^2_k I\right)_{k_0} = c(1-c)I^2(k_0)\left(\partial^2_k \Sigma - 2\beta \partial^2_k V\right)_{k_0}. \tag{3}$$

The splitting therefore disappears when curvatures of the self-energy and of the interaction term at the SP $k_0$ compensate each other:

$$2\left(\partial^2_k V\right)_{k_0} = T\left(\partial^2_k \Sigma\right)_{k_0}. \tag{4}$$

To analyse qualitatively the behaviour of the splitting close to the coalescence point, it is convenient to use the analogy with the Landau theory of second-order phase transitions (e.g., Landau and Lifshitz 1980). In this temperature range the splitting above $T_0$ is small, and expansions of $V(k)$ and $\Sigma(k)$ in powers of the deviation $\delta k = k - k_0$ of the wavenumber from the SP $k_0$ can be used. To describe the split minimum of $V(k)$, only the second- and fourth-order terms are needed; since a SP serves as the origin, the expansions do not contain odd powers of $\delta k$. It is therefore assumed that in the area of the splitting $V(k)$ and $\Sigma(k)$ have the following approximate form,

$$f(k) = f(0) + a_f(\delta k)^2/2 + b_f(\delta k)^4/4, \tag{5}$$

where $f = V, \Sigma$, $a_V < 0$, $b_V > 0$, $a_{\Sigma} < 0$ ($\Sigma(k)$ has a maximum at $k = k_0$), and the sign of $b_{\Sigma}$ is arbitrary. Substituting Eqs. (3) for $V$ and $\Sigma$ into Eq. (3), we get the same expression (3) for the inverse intensity $G = I^{-1}$, where at $T = T_0$ the second-order coefficient $a_G = c(1-c)(-a_{\Sigma} + 2\beta a_V)$ vanishes (see Eq. (3)), while the fourth-order one $b_G$ remains positive. In the vicinity of $T_0$ we can then write $a_G = \tilde{a}_G(T - T_0)$, $\tilde{a}_G < 0$ and regard $b_G$ as temperature-independent. The inverse intensity $I^{-1}(k)$ thus behaves in almost the same way as the Landau free energy, and $\delta k$ is the analogue of the order parameter. The only difference here is that the role of temperature is reversed: $I^{-1}(k)$ has a double
minimum above the coalescence temperature $T_0$ and a single one below it. From this analogy it follows that the splitting increases with temperature as $(T - T_0)^{1/2}$ at small positive values of $T - T_0$. Unlike its Landau-theory counterpart, the obtained bifurcation exponent $s = 0.5$ is exact, since the intensity is a regular function of the wavevector expandable into the Taylor series. At higher temperatures the behaviour of the splitting changes, and its value starts to approach that of the splitting in $V(k)$. In this regime the difference between the two decreases with temperature as $1/T$, unless the alloy is equiatomic, in which case the decrease is faster (Tsatskis 1998a).

Returning to the quantitative description of the temperature dependence of the splitting in the whole range of temperatures, we note that it can be considerably simplified by taking account of the particular behaviour of $V(k)$ and $\Sigma(k)$ (Tsatskis 1998a). The Fourier transform $F(k)$ of an arbitrary real-space matrix $F$ defined on the FCC lattice varies with $k$ as follows: 1st coordination shell does not contribute to its $k$-dependence; 2nd and higher shells lead to the term proportional to $\cos 2\pi k$; starting from 8th shell, $\cos 4\pi k$ term appears; 21st shell produces $\cos 6\pi k$ term, etc. Here $k$ is defined as the deviation from the SP X and measured in the reciprocal-lattice units (r.l.u.). As a result, under the assumption that matrix elements of $F$ beyond 20th coordination shell are of no importance,

$$F(k) = A_F + 2B_F \cos 2\pi k + 2C_F \cos 4\pi k,$$

where the coefficients are linear combinations of the matrix elements $F_{ij}$; for explicit expressions for the relevant quantities $B_F$ and $C_F$, see Tsatskis (1998a). To find the $I(k)$ peak positions, we insert Eqs. (6) for $V$ and $\Sigma$ into Eq. (4) for the $I(k)$ extrema. The presence of the off-SP minima in $V(k)$ implies $C_V > 0$, $|B_V| < 4C_V$, while the assumption of the absence of such extrema in $\Sigma(k)$ requires $|B_\Sigma| > 4|C_\Sigma|$. The positions $k_I$ of the intensity peaks away from the SPs above $T_0$ are given by

$$\cos 2\pi k_I = -\frac{(2B_V - TB_\Sigma)/4}{(2C_V - TC_\Sigma)},$$

whereas the $V(k)$ minima $k_V$ can be obtained from Eq. (7) by putting $B_\Sigma = C_\Sigma = 0$. Substituting the same Eqs. (6) into Eq. (4), we obtain a simpler equation for the coalescence temperature $T_0$,

$$2(\pm B_V + 4C_V) = T_0 (\pm B_\Sigma + 4C_\Sigma),$$

where upper and lower signs correspond to the coalescence at the SPs X and W, respectively. Contrary to Eq. (8), the explicit expression for $T_0$ cannot be obtained, since $B_\Sigma$ and $C_\Sigma$ are temperature-dependent.

To calculate $B_\Sigma$ and $C_\Sigma$, a particular approximation for SRO must be used. Here we turn to the simplest theory leading to the wavevector dependence of the self-energy, the high-temperature expansion (HTE) (Tsatskis 1998a,b). The HTE is the expansion in powers of $\beta V$; the second-order HTE approximation for the self-energy gives

$$\Sigma(k) = \Sigma_d + 2x\beta^2 W(k),$$

where $x = (1 - 2c)/2$, $W_{ij} = V_{ij}^2$, and $\Sigma_d$ is the diagonal part of the self-energy in the site representation which does not contribute to the $k$-dependence of $\Sigma$. Then

$$B_\Sigma = 2x\beta^2 B_W, \quad C_\Sigma = 2x\beta^2 C_W,$$
FIG. 3. Positions of the intensity peaks versus dimensionless temperature \( t = 4C_V T / |B_W| \) for the A\(_3\)B alloy with the interaction \( V(\mathbf{k}) \) such that \( C_W = 0 \) and \( k_V = 0.25 \) (i.e., the minima of \( V(\mathbf{k}) \) are located half-way between SPs X and W). For this set of parameters \( t_{X}^{0} = t_{W}^{0} = 0.25 \), and the character of the temperature dependence of the splitting is defined by the sign of \( B_W \): (a) \( B_W > 0 \), case (i) in the text, (b) \( B_W < 0 \), case (ii).

where \( |B_W| > 4|C_W| \). Substitution of Eqs. (10) into Eq. (7) leads to the result

\[
\cos 2\pi k_I = - \frac{(B_V - x\beta B_W)}{4(C_V - x\beta C_W)} .
\]

Calculation of the temperature derivative shows that in this approximation the behaviour of the splitting is determined by the sign of the \( T \)-independent quantity \( B_W C_V - B_V C_W \):

\[
\partial_\beta (\cos 2\pi k_I) = \frac{x(B_W C_V - B_V C_W)}{4(C_V - x\beta C_W)^2} .
\]

(i) \( B_W C_V > B_V C_W \): The derivative (12) is positive, and \( \cos 2\pi k_I \) increases with decreasing temperature; the intensity peaks move away from the \( V(\mathbf{k}) \) minima and towards the SP X (Fig. 3(a)). Finally, the peaks coalesce at X when \( \cos 2\pi k_I \) reaches the value +1 at the bifurcation point

\[
T_0^X = x \frac{(B_W + 4C_W)}{(B_V + 4C_V)} .
\]

(ii) \( B_W C_V < B_V C_W \): The intensity peaks shift towards the SP W (Fig. 3(b)). The splitting disappears when \( \cos 2\pi k_I = -1 \), i.e., at the temperature

\[
T_0^W = x \frac{(B_W - 4C_W)}{(B_V - 4C_V)} .
\]

(iii) \( B_W C_V = B_V C_W \), or the alloy is equiatomic \( (c = 0.5) \): The derivative (12) vanishes and the second-order HTE approximation predicts temperature-independent splitting. In this situation the temperature behaviour of the splitting is defined by the third- and higher-order terms in the HTE for the self-energy.

The predicted coalescence of the FS-related intensity peaks can, in principle, be described by using any theory of SRO which leads to the \( \mathbf{k} \)-dependent self-energy. As was already noted, the frequently used KCM and SM approximations fail to reproduce this feature of the exact self-energy. Apart from the HTE, the available theories include the cluster variation method (CVM) (Kikuchi 1950, 1951), the \( \gamma \)-expansion method (GEM) (Tokar 1985, Tokar, Masanskii and Grishchenko 1990, Masanskii, Tokar, and Grishchenko 1991), and the \( \alpha \)-expansion (AE) (Tsatskis 1998a) closely related to the GEM. The corresponding approximations for the self-energy were compared by Tsatskis (1998b). However, the CVM is a direct-space method and as such is hardly applicable to the case of long-range interactions. To describe the off-SP minima of \( V(\mathbf{k}) \), at least eight first potentials are needed, and accurate sets of inverse Monte Carlo (MC) interactions determined from experimental data are yet significantly larger (Schönfeld et al. 1996). The HTE approach is limited to the same extent as the KCM approximation; it leads to quantitatively correct results only at sufficiently high temperatures, as follows from its very name. The GEM utilizes the assumption about rapid decrease of interatomic correlations with distance, which is invalid for long-range interactions. This leaves the AE, a modification of the GEM specifically designed to be used in such cases (Tsatskis 1998a). Similarly to the GEM, the AE is expected to be sufficiently accurate at realistic temperatures.
We now compare the effect of the coalescence with another anomaly in the SRO scattering, the “thermal” splitting of the intensity peak, observed for the Pt-V alloy system and reproduced in the MC simulations (Le Bolloc’h, Cren, Caudron and Finel 1997). For this system, the (100) peak splits along the (100) line with increasing Pt content. A theory of this anomaly was proposed by Tsatskis (1998c), who also showed that the splitting can occur when temperature decreases at fixed composition. This prediction was confirmed by the MC calculations (Le Bolloc’h 1997), though the effect has not yet been observed experimentally. According to the proposed theory, the thermal splitting can be explained by the same mechanism of the compensation at the SP of the $\Sigma(k)$ (1997), though the effect has not yet been observed experimentally. According to the proposed theory, the thermal splitting can be explained by the same mechanism of the compensation at the SP of the $\Sigma(k)$ and $2\beta V(k)$ curvatures. However, in this case the interaction $V(k)$ has a simple minimum at the corresponding SP and, in agreement with the mean-field arguments, produces the $I(k)$ peak with no fine structure at higher temperatures. This peak splits as temperature decreases and the positive curvature of $\Sigma(k)$ exceeds that of $2\beta V(k)$. In the event of the coalescence, on the other hand, the fine structure of $V(k)$ is erased at lower temperatures due to the growing negative $\Sigma(k)$ curvature. Both phenomena can be conveniently described within the same Landau-type approach outlined above. The only formal difference is the sign of $\tilde{a}_G$: $\tilde{a}_G > 0$ for the thermal splitting and $\tilde{a}_G < 0$ for the coalescence.

The present theory shows that the coalescence temperature $T_0$ does not, in general, coincide with the transition temperature $T_t$ and is more or less arbitrary. Nevertheless, it can accidentally be close to $T_t$ (unless the ordering transition occurs first). This is a possible reason for the rather good agreement between the theoretical value $s = 0.5$ of the bifurcation exponent and the experimental result $s = 0.38 \pm 0.15$ obtained for the Cu$_3$Au alloy (Reichert et al. 1996). The remaining discrepancy can be attributed to the difference between $T_0$ and $T_t$, and also to the data fitting over the wide temperature interval (about 140 K).

Finally, we note that the proposed mechanism of the curvature compensation explains also the results obtained for the exactly solvable 1D Ising model with nearest- and next-nearest-neighbour interactions (Kulik, Gratias and de Fontaine 1989) and for the 2D ANNNI model in the framework of the CVM (Finel and de Fontaine 1986). Observed for these two models is, in fact, the same effect of the coalescence as described here: the $I(k)$ peaks produced by the off-SP minima of $V(k)$ move towards a SP as temperature decreases and transform at this SP into a single peak at some temperature before the onset of long-range order (for the 1D model, at non-zero temperature). The exact solution in the former and the CVM in the latter case lead to the $k$-dependent self-energy whose SP curvature compensates that of the interaction term at the coalescence temperature. In all three cases the real-space interactions produce minima off SPs in the reciprocal space; however, Finel and de Fontaine (1986) and Kulik et al. (1989) considered the short-range competing interactions which are very different from the long-range interactions associated with the FS effects.

In summary, we have pointed out a possibility for the FS-related splitting of the SRO intensity peak to disappear at some temperature above the order-disorder transition. The off-SP intensity peaks reflecting corresponding minima of the effective pair interaction in the $k$-space can move towards one of the SPs (X or W) as temperature decreases and eventually coalesce at this SP, transforming themselves into a single peak. The driving force behind this effect is the $k$-dependence of the self-energy which becomes stronger with decreasing temperature. The coalescence occurs when the self-energy and interaction curvatures at the SP compensate each other. The shift of the intensity peaks with decreasing temperature towards X (an increase of the splitting with temperature) was observed for the Cu$_3$Au alloy (Reichert et al. 1996), while neither the shift towards W (a decrease of the splitting with temperature) predicted by Tsatskis (1998a) nor the coalescence at any of these SPs were found. The coalescence can be described qualitatively by the Landau-type theory and quantitatively by any theory of SRO which is sufficiently accurate and leads to the wavevector dependence of the self-energy. This excludes two popular approximations, the KCM and the SM, in which the self-energy is site-diagonal. The effect of the coalescence has been compared with the “thermal” splitting of the SRO intensity peak which was observed experimentally and in the MC simulations and can be described within the same theoretical framework.
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