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LETTER TO THE EDITOR

Theory of the temperature dependence of the Fermi-surface-induced splitting of the alloy diffuse-scattering intensity peak

Igor Tsatskis†

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK

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Abstract. An explanation is presented for the temperature dependence of the fourfold intensity peak splitting found recently in the diffuse x-ray scattering from the disordered Cu₃Au alloy. The wavevector and temperature dependence of the self-energy is identified as the origin of the observed behaviour. Two approaches for the calculation of the self-energy, the high-temperature expansion and the α -expansion, are proposed. Applied to the Cu₃Au alloy, both methods predict an increase of the splitting with temperature, in agreement with experimental results.

Recently, in the first *in situ* experiment to resolve the fine structure of the equilibrium x-ray diffuse-scattering intensity from the disordered Cu₃Au alloy, Reichert, Moss and Liang [1] observed a marked temperature dependence of the fourfold splitting of the (110) short-range order (SRO) diffuse intensity peak. The separation of the split maxima changed reversibly, increasing with temperature. The same behaviour of the splitting was also found in [2] by analysing the results of Monte Carlo (MC) simulations for the Cu_{0.856}Al_{0.144} alloy [3]. The peak splitting (figure 1) is attributed to the indirect interaction of atoms via conduction electrons in an alloy whose Fermi surface has flat portions; the effective interatomic pair interaction itself has split minima in the reciprocal space, and their location is determined by the wavevector $2\mathbf{k}_F$ spanning these flat portions of the Fermi surface [4]. As indicated in [1], current theoretical approaches fail to explain the observed behaviour. Indeed, the standard approximation for the SRO diffuse intensity, the Krivoglaz–Clapp–Moss (KCM) formula [5], is

$$I^{KCM}(\mathbf{k}) = \frac{1}{1 + 2c(1 - c)\beta V(\mathbf{k})} \quad (1)$$

where $I(\mathbf{k})$ is the intensity in Laue units, c is the concentration, $\beta = 1/T$, T is the temperature in energy units and $V(\mathbf{k})$ the Fourier transform of the combination $V_{ij} = (V_{ij}^{AA} + V_{ij}^{BB})/2 - V_{ij}^{AB}$ of the potentials $V_{ij}^{\alpha\beta}$ with which an atom of type α at site i interacts with an atom of type β at site j . Equation (1) predicts that the positions of the $I(\mathbf{k})$ peaks coincide with those of the corresponding minima of $V(\mathbf{k})$; therefore, the splitting does not depend on T , if it is assumed that $V(\mathbf{k})$ is T -independent. This assumption is justified at least as far as positions of the $V(\mathbf{k})$ minima are concerned, since the value of $2\mathbf{k}_F$ should not change over the temperature range considered [1]. Also, the MC calculations [3] in which the increase of the splitting with temperature was found [2]

† E-mail: it10001@cus.cam.ac.uk; former name: I V Masanskii.

were carried out for T -independent pair interaction parameters. On the other hand, the cluster variation method [6], which in most cases leads to a significant improvement of the results in comparison with the KCM approximation [7], is practically inapplicable here, since interactions between atoms at distant lattice sites are involved (see below).

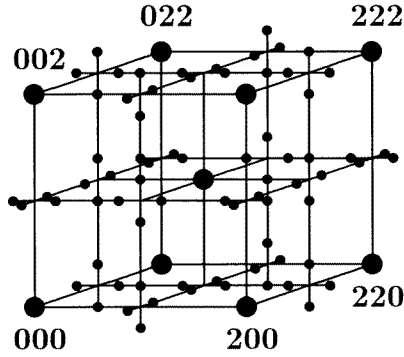


Figure 1. A schematic reciprocal-space picture of the scattering from the FCC alloys discussed in the text. Large circles represent the Bragg reflections, while small ones (forming characteristic crosses) correspond to the split diffuse intensity peaks.

The aim of the present letter is to propose a theory for the temperature-dependent peak splitting observed for the Cu_3Au alloy. We begin by noting the exact expression for the SRO diffuse-scattering intensity [8]:

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

where $\Sigma(\mathbf{k})$ is the so-called self-energy which depends not only on \mathbf{k} , but also on c and T . In the KCM approximation, however, Σ is \mathbf{k} - and T -independent, as follows from comparison of equations (1) and (2):

$$\Sigma^{KCM} = -[c(1-c)]^{-1}. \quad (3)$$

Below, we consider the $I(\mathbf{k})$ profile along one of the lines containing split peaks, e.g., the $(h10)$ line, and concentrate on two peaks around the (110) position. The peak positions k_I (k is the deviation of the wavevector from the (110) position along the $(h10)$ line) are determined by the condition $\partial_k I = 0$, which gives

$$2 \partial_k V = T \partial_k \Sigma. \quad (4)$$

Equation (4) means that the \mathbf{k} -dependence of Σ leads to a shift $\delta k = k_I - k_V$ of the peak position with respect to the position k_V of the corresponding minimum of $V(\mathbf{k})$ (figure 2); k_V is the solution of the equation $\partial_k V = 0$. Furthermore, the right-hand side of equation (4) is a function of T , while its left-hand side is T -independent. The $I(\mathbf{k})$ peaks will therefore change their positions with temperature.

At sufficiently high temperatures the behaviour of the splitting can be analysed by using the high-temperature expansion (HTE, in powers of βV) for Σ . The second-order HTE approximation gives [9]

$$(\Sigma_d)_{ii} = \Sigma^{KCM} - 4c(1-c)\beta^2 \sum_l V_{il}^2 \quad (5a)$$

$$(\Sigma_{od})_{ij} = 2(1-2c)^2 \beta^2 V_{ij}^2. \quad (5b)$$

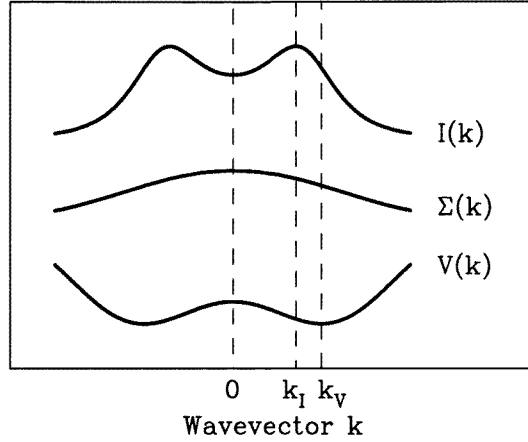


Figure 2. The shift of the intensity peak position as a result of the wavevector dependence of the self-energy. The latter is as found for the Cu_3Au alloy (see the text).

Here Σ_d is the diagonal and Σ_{od} the off-diagonal part of Σ . In this approximation equation (4) reduces to

$$\partial_k V = (1 - 2c)^2 \beta \partial_k W \quad W_{ij} = V_{ij}^2. \quad (6)$$

The right-hand side of equation (6) is small due to the prefactor β , and its solution k_I deviates little from k_V . It is then sufficient to expand $\partial_k V$ and $\partial_k W$ in powers of the shift δk and retain only linear terms:

$$\partial_k V(k) = (\partial_k^2 V)_{k_V} \delta k \quad (\partial_k^2 V)_{k_V} > 0 \quad (7a)$$

$$\partial_k W(k) = (\partial_k W)_{k_V} + (\partial_k^2 W)_{k_V} \delta k. \quad (7b)$$

Substituting equations (7) into equation (6) and neglecting the last term in equation (7b) because of the smallness of the right-hand side of equation (6) leads to the result

$$\delta k = (1 - 2c)^2 (\partial_k W)_{k_V} / T (\partial_k^2 V)_{k_V}. \quad (8)$$

Equation (8) represents two scenarios for the temperature dependence of the splitting, depending on the sign of $(\partial_k W)_{k_V}$. The first is the increase of the splitting with temperature discussed above. For the second the theory predicts that a decrease of the splitting with increasing temperature is also possible; such a temperature dependence has not yet been observed. The absolute value of δk decreases as T^{-1} with temperature. The shifts of the two peaks have opposite signs and the same absolute values, and the wavevector dependence of Σ determines whether the splitting increases or decreases with temperature. In the case of an equiatomic alloy ($c = 0.5$) the second-order contribution to $\partial_k \Sigma$ is zero, and the temperature behaviour of the shift is defined by the higher-order terms in the HTE for the self-energy.

We now apply the HTE to the Cu_3Au alloy, for which sets of the first eight inverse MC interactions V_{lmn} were obtained at different temperatures using the SRO parameters α_{lmn} available in the literature [10]. Despite its extended range, the behaviour of the interaction along the $(h10)$ line is simple; the Fourier transform $f(\mathbf{k})$ of an arbitrary FCC matrix f_{ij} with non-zero elements for the first 20 coordination shells lmn has along this line the form

$$f(k) = A_f + 2B_f \cos 2\pi k + 2C_f \cos 4\pi k \quad (9)$$

Table 1. The coefficients B_f and C_f (equations (10)) for the interaction $V(k)$ and the related function $W(k)$ as calculated from the inverse MC interactions V_{lmn} [10] for the Cu_3Au alloy at different temperatures.

No	T (K)	B_V (meV)	C_V (meV)	B_W (meV ²)	C_W (meV ²)
1	669	-11.2	4.3	974.8	18.6
2	678	-11.9	2.8	202.6	8.1
3	693	-7.5	3.9	93.8	15.0
4	723	-3.8	0	131.6	0
5	748	-22.8	3.4	297.9	11.9
6	958	6.7	0	-13.7	0
7	958	-71.7	3.1	1657.1	9.6
8	1023	17.7	2.1	285.7	4.3

where the relevant coefficients B_f and C_f are

$$B_f = f_{200} - 4f_{211} + 4f_{220} + 4f_{222} - 8f_{321} + 4f_{420} - 4f_{332} + 8f_{422} - 8f_{521} + 4f_{442} \quad (10a)$$

$$C_f = f_{400} - 4f_{411} + 4f_{420} + 4f_{422} - 8f_{431} + 4f_{440} - 4f_{433} + 8f_{442} \quad (10b)$$

and k is measured in reciprocal-lattice units (r.l.u.). These coefficients for the functions $V(k)$ and $W(k)$ are shown in table 1. All four quantities scatter widely, which is a result of the relatively low accuracy of the inverse MC interactions for the Cu_3Au alloy discussed in [10]. In particular, the accuracy and/or number of interactions are insufficient for the correct description of the split minimum of $V(k)$. The splitting in $V(k)$ occurs when $C_V > 0$ and $|B_V| < 4C_V$, and this is so only for sets 1 and 3. In cases 4 and 6, $C_V = 0$, since the eighth interaction V_{400} (the only one contributing to C_V) was not included in the corresponding sets. In addition, for cases 6 and 8, $B_V > 0$, so the split minimum would occur around the $(\frac{1}{2}10)$ rather than the (110) position. Nevertheless, despite the low accuracy, it is seen that B_W is positive and C_W is non-negative. The only exception is set 6, where B_W acquires a very small negative value. However, the second set of interactions (set 7, with non-zero V_{400}) obtained using the same SRO parameters leads to positive values of both B_W and C_W . In the case where $B_W > 0$, $C_W \geq 0$, the function $W(k)$ has a maximum at the (110) position which is much wider than the magnitude of the peak splitting; the $|k_f|$ values observed in [1] were quite small (less than 0.1 r.l.u.). As a result, the derivative $\partial_k W$ is positive for the left-hand and negative for the right-hand minimum of $V(k)$ (figure 2), and at any finite temperature the intensity peaks are shifted towards the (110) position. The absolute value of the shift increases with decreasing temperature, so the splitting increases with temperature.

The applicability of the HTE, similarly to that of the KCM approximation, is limited to the case of sufficiently high temperatures. To deal with moderate temperatures, we introduce here another approach which leads to k - and T -dependence of Σ , namely its expansion in powers of the SRO parameters α_{ij} (hereafter the α -expansion, or AE). Two non-zero orders of the AE for Σ_{od} were calculated [8] in the framework of the γ -expansion method (GEM) [8, 11]:

$$(\Sigma_{od})_{ij} = a\alpha_{ij}^2 + b\alpha_{ij}^3 + O(\alpha^4) \quad (11a)$$

$$a = \frac{(1-2c)^2}{2[c(1-c)]^2} \quad (11b)$$

$$b = \frac{[1-6c(1-c)]^2 - 3(1-2c)^4}{6[c(1-c)]^3}. \quad (11c)$$

The expression for Σ_d then comes from the sum rule

$$\alpha_{ii} = \Omega^{-1} \int d\mathbf{k} I(\mathbf{k}) = 1 \quad (12)$$

(here the integration is carried out over the Brillouin zone of volume Ω), equation (12) being one of the AE (or GEM) equations:

$$(\Sigma_d)_{ii} = \Sigma^{KCM} + 2\beta \sum_j V_{ij} \alpha_{ij} - \sum_{j(\neq i)} (a\alpha_{ij}^3 + b\alpha_{ij}^4) + O(\alpha^5). \quad (13)$$

Note that the sum of the first two terms corresponds to the spherical model (SM) for SRO [12], which is the zero-order approximation for the AE and GEM; in the SM, the self-energy is diagonal ($a = b = 0$). The difference between the AE and GEM lies in the choice of the expansion parameter(s). The GEM parameter is $\gamma = \exp(-1/\xi)$, ξ being the dimensionless correlation length, and terms in the diagrammatic expansion for the self-energy are selected according to the total length of all of the lines in the diagrams, where the line connecting sites i and j represents α_{ij} . The GEM is based on the assumption that the correlations decrease rapidly with distance; this assumption is invalid here because distant interactions are essential. The AE uses the α_{ij} themselves as the expansion parameters; the terms are chosen according to the number of lines in the diagrams (i.e., the powers of α_{ij}), since all of the α_{ij} are sufficiently small. The GEM was successfully applied to both the direct and inverse problems of alloy diffuse scattering [8, 13], leading to reliable results everywhere except in the vicinity of the instability point. On the basis of our experience with the GEM, we can also expect the AE to be quite accurate at almost all temperatures.

Table 2. The AE coefficients B_f and C_f (equations (10)) for the self-energy $\Sigma(k)$ as calculated within the ten-shell approximation (except for set 16; see the text) from the experimental sets of SRO parameters for the Cu₃Au alloy at different temperatures.

No	T (K)	B_Σ	C_Σ	Reference
1	669	0.1742	0.0079	[14]
2	693	0.0905	0.0119	[14]
3	748	0.0915	0.0013	[14]
4	958	0.0268	0.0022	[14]
5	1023	0.0231	0.0002	[14]
6	669	0.2172	0.0194	[15]
7	693	0.0787	0.0141	[15]
8	748	0.0592	0.0035	[15]
9	958	0.0130	0.0042	[15]
10	1023	0.0120	0.0006	[15]
11	678	0.2086	0.0060	[16]
12	733	0.1372	0.0004	[16]
13	823	0.0530	0.0006	[16]
14	678	0.4137	0.0144	[17]
15	723	0.2053	0.0037	[17]
16	678	0.1791	0	[18]
17	703	0.0911	0.0021	[19]

Applying the AE to the Cu₃Au alloy, we calculate the coefficients B_Σ and C_Σ combining equations (10) and (11) and using available sets of experimental SRO parameters [14–19]. Their values for the case of the first ten shells included in the AE approximation (11) for the self-energy are given in table 2 (a five-shell AE approximation was used for set 16, since only five SRO parameters were determined in [18]). Inclusion of additional shells

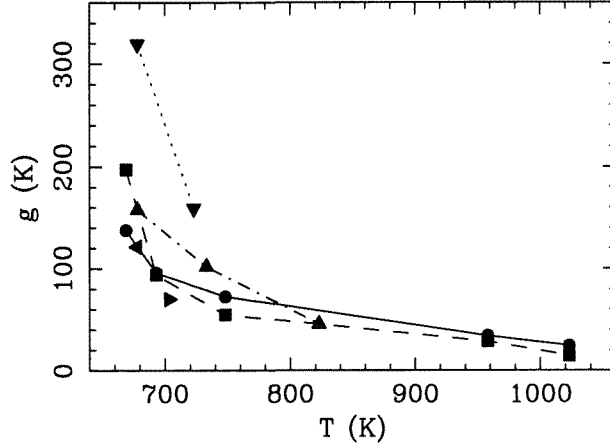


Figure 3. Values of g (equation (14)) versus temperature calculated using the data from table 2: [14]: dots, solid line; [15]: squares, dashed line; [16]: upward-pointing triangles, chain line; [17]: downward-pointing triangles, dotted line; [18]: leftward-pointing triangle; [19]: rightward-pointing triangle.

does not alter the results. In all cases B_Σ is positive and C_Σ is non-negative, so, as before, $\Sigma(k)$ has a maximum at the (110) position which is very wide in comparison with the peak splitting, and the intensity peaks are shifted towards this position. Contrary to the case for the HTE, the explicit temperature dependence of the AE self-energy is unknown, since the SRO parameters in equations (11) are complicated functions of temperature. To find the temperature behaviour of the splitting, we use the data from table 2 and plot in figure 3 against temperature the quantity

$$g = T \left| \partial_k^2 \Sigma \right|_{k=0} / 8\pi^2 = T(B_\Sigma + 4C_\Sigma) \quad (14)$$

which characterizes the temperature dependence of the right-hand side of equation (4) at small k . It is seen that g is a decreasing function of T , which corresponds to the increase of the splitting with temperature. Its temperature dependence is particularly strong in the range below 800 K, where the intensity profile was measured in [1].

To summarize, we have presented an explanation of the temperature dependence of the Fermi-surface-induced diffuse intensity peak splitting found recently for the Cu_3Au alloy. The wavevector and temperature dependence of the self-energy is understood to be the origin of this behaviour. The proposed theory is able to describe the observed increase of the peak separation with temperature; in addition, it also predicts the possibility of the splitting decreasing as temperature increases, a behaviour which has not yet been found. Two methods for the calculation of the k - and T -dependent self-energy, the HTE and the AE, have been proposed. Applied to the existing experimental and inverse MC data for the Cu_3Au alloy, both methods predict the increase of the splitting with temperature, in agreement with the experimental findings. However, the HTE is not expected to be reliable when applied to alloys at realistic temperatures, so the AE approach is preferable. Despite the seeming complexity of the problem (the interaction involves many coordination shells), the theoretical analysis proves to be surprisingly simple.

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