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Compton scattering studies of charge transfer in Co–Ni amorphous alloys

E Zukowski†¶, L Dobrzynski†, M J Cooper‡, D N Timms‡, R S Holt§ and J Latuszkiewicz‖

† The Faculty of Physics, Warsaw University Branch, 15-424 Bialystok, Lipowa 41, Poland

‡ Department of Physics, University of Warwick, Coventry CV4 7AL, UK

§ Rutherford Appleton Laboratory, Oxon OX11 0QX, UK

‖ Institute of Material Science and Engineering, Warsaw University of Technology, Warsaw, Narbutta 85, Poland

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Abstract. The electron momentum density in four amorphous alloys of composition $Co_{70-x}Ni_xFe_5Si_{15}B_{10}$ (x = 0, 10, 40 and 55) has been studied in Compton scattering experiments using 412 keV γ-radiation. The results indicate that the replacement of cobalt by nickel in these alloys is associated with a transfer of charge density from the 4s to the 3d band, which is consistent with their magnetic behaviour.

1. Introduction

1.1. The magnetic moment in nickel-based amorphous alloys

Amorphous magnetic materials are of interest to physicists from both fundamental and practical viewpoints. Their macroscopic properties are isotropic whereas on the microscopic level the magnetic moments, electronic density of states etc depend on the details of the local order, all of which make the *ab initio* description still very difficult to achieve.

Experimental studies of magnetic moments in amorphous metals have provided much information on the dependence of magnetic moments on the type and number of surrounding atoms; reviews of such studies can be found in [1–3]. The proper interpretation of the origin of the magnetic moments, however, still remains an open question. For example, in relation to amorphous nickel alloys containing more than about 20 at.% of metalloid atoms there exist papers in which the magnetic moment is claimed to reside on nickel atoms—see e.g. [4, 5]—and there are others in which nickel is considered to possess no moment—e.g. [6]. In ordered, as well as in disordered alloys, nickel usually assumes a magnetic moment; it is therefore difficult to understand why it may lose it, partially or completely, when it becomes a constituent of an amorphous alloy. The magnetic moments of iron, cobalt and nickel are generally smaller in amorphous materials (containing almost as a rule metalloid atoms: B, Si, P etc) than in the crystalline

¶ Current address: Department of Physics, University of Warwick, Coventry CV4 7AL, UK.

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alloys. The most frequently proposed explanation of this is based on the rigid-band model in which the metalloid atoms are supposed to add their valence electrons to the 3d band [7]. Although this interpretation is attractive, the rigid-band model actually fails when applied to crystalline alloys as far as individual magnetic moments of atoms are concerned. Therefore its application to amorphous metals needs to be treated with some caution, and more attention paid to the hybridisations of d and sp bands [8].

The results of studies of the concentration dependence of the magnetic moment in $(Co_{1-x}Ni_x)_{75}P_{16}B_6Al_3$ alloys [6] have been interpreted on the assumption that nickel carries no magnetic moment. In the light of measurements on $Co_{70-x}Ni_xFe_5Si_{15}B_{10}$ [9], nickel should assume a magnetic moment of the order of $0.05\,\mu_B$. This moment is eventually lost when the nickel concentration is high enough.

The enormous complexity of amorphous materials challenges theorists to devise sophisticated models and tractable mathematical methods. In developing them a wide range of information on microscopic properties is often needed either as an input to the theory or as a test of the correctness of the procedure. In particular, it is interesting to ask how the valence electrons of the alloy constituents behave. What is their spatial distribution? How well are they localised? To answer these and other questions, information on charge, spin and momentum density distributions is very helpful.

The studies of Co-based amorphous alloys in which cobalt is systematically substituted by nickel are important for a proper understanding of the electronic structure because such studies allow investigations of the effects caused by a single d electron added to the system. The existence of the charge transfer from the metalloid atom to the transition metal atom seems to be supported by Compton profile studies of Ni–P, Co–P [10] and Ni–B [11] alloys.

1.2. Compton scattering studies of the electron momentum density

In Compton scattering experiments the Compton profile, $J(p_z)$, which is a one-dimensional projection of the electron momentum density, $n(\boldsymbol{p})$, is derived directly from the spectral distribution of the inelastically scattered radiation, i.e.

$$\frac{d^2\sigma}{d\Omega\, d\omega} \propto J(p_z) = \int\int n(\boldsymbol{p})\, dp_x\, dp_y \tag{1}$$

where the z axis is parallel to the photon scattering vector. This relationship holds within the impulse approximation which requires that the energy transfer is large compared with the electron binding energies in the target. This is certainly valid when the 412 keV photons used in this study are scattered through 167° because the mean energy transfer is 253 keV and the line shape is restricted to a 22 keV range. Details of the Compton scattering technique and its application to the study of electron momentum density distributions can be found in [12] and [13]. Despite the integration over two dimensions of momentum space the line shape retains sufficient sensitivity to the behaviour of the outer (slow-moving) conduction electrons to act as a critical test of specific band theories and their underlying assumptions.

Many Compton scattering studies, making use of the ^{198}Au radioisotope emission at 412 keV, have been performed over the last decade by groups based at Warwick University and the Hahn–Meitner Institut in Berlin. During the course of measurements on Cr [14], Fe [15], Ni [16] and Cu [17], the analysis of line shape data has been refined to such a level that absolute profiles can be confidently interpreted at a significance level well below 1% of the Compton peak height (in the joint study of nickel referenced above

a precision of 0.2% $J(0)$ was demonstrated). These were all studies of single crystals which can take advantage of the directional nature of $J(p_z)$ to isolate the aspherical part associated with the outer conduction electron density and remove the spherical core contribution which is of less interest, being well modelled by well documented free-atom wave-functions [18]. This separation is effectively achieved by forming pairs of directional profiles: $\Delta J(p) = J_{hkl}(p) - J_{h'k'l'}(p)$. It has the great benefit of eliminating the many systematic errors that affect individual profiles.

Obviously that particular approach cannot be used in amorphous metals, but a difference method can still be used to advantage. For example, in the previous Compton scattering studies of amorphous metals by Itoh and co-workers in Japan [10, 11, 19] the differences between the crystalline and amorphous phases have been interpreted as providing evidence for the delocalisation of charge density in the latter. In the present investigation the materials contain five atomic species, three of which are invariant. It was therefore essential to form difference profiles in order to isolate the changes that occur when nickel is substituted for cobalt.

2. The measurements

The experiments were performed on the ^{198}Au Compton spectrometer sited at the Rutherford Appleton Laboratory. The instrument was originally described in [20] and recent examples of its use can be found elsewhere [14, 15, 16]. Two gold sheets, each 1 mm thick and 6 mm × 4 mm in area are sandwiched together in a graphite holder to form the source, which is irradiated to an activity of approximately 150 Ci. The dominant 412 keV γ-ray line results from a decay with a half-life of 2.7 days, which necessitates using a fresh source every two weeks. The scattering angle of the instrument is fixed at 167° and the scattered radiation is recorded by an intrinsic germanium detector coupled to a 4096-channel analyser.

The four amorphous alloy samples were prepared by rapid quenching on a copper roller as ribbons of width 10–15 mm and thickness 33 ± 5 μm. The densities were determined [9] to be 7,710 ± 50 kg m^{-3} and x-ray inspection revealed a negligible volume of crystalline inclusions. The ribbons were wrapped around a nylon former and clamped to produce a rectangular sample of thickness adequate to ensure a count rate of at least 50 counts per second and a peak-to-background ratio of 100 : 1; in practice this meant at least 1 mm, i.e. 30 layers. The frame and clamps were well outside the circular area of 250 mm^2 illuminated by the beam. Each spectrum was accumulated over a 50–120 h period to yield an integrated Compton intensity of ~10^7 photons. Three sources were used, two samples being measured with each so that any systematic effects associated with a particular source could be eliminated in a difference plot. Time permitted the repetition of measurements on two of the four samples only.

Electronic drift was checked by monitoring the position of the 122 keV ^{57}Co line from a calibration source, but no drift greater than the energy width of the analyser bin (50 eV) was detected. The detector resolution, which had been characterised in previous studies (see, for example, [21]), was equivalent to 0.40 au of electron momentum (1 au = 1.99 × 10^{-24} kg m s^{-1}). Other details of the measurements are collated in table 1.

3. Data analysis

The data processing requires the transformation of the observed spectrum into a function of the momentum of the target electron, i.e. the Compton profile in equation (1); it

Table 1. Experimental details.

Sample	Dimensions (mm × mm × mm) (length × width × thickness)	Measurement time (h)	Integrated Compton counts
S1† $Co_{70}Ni_0Fe_5Si_{15}B_{10}$	20 × 10.0 × 2.20	91	58×10^6
S2 $Co_{60}Ni_{10}Fe_5Si_{15}B_{10}$	20 × 14.5 × 1.25	50	8×10^6
S3 $Co_{30}Ni_{40}Fe_5Si_{15}B_{10}$	20 × 14.5 × 1.45	116	9×10^6
S4† $Co_{15}Ni_{55}Fe_5Si_{15}B_{10}$	20 × 12.0 × 2.20	216	57×10^6

† Samples irradiated twice with different gamma sources. Measurement times and integrated Compton counts are each sums of two data sets.

comprises a string of corrections, the most problematical of which are those for the detector response function and the multiple-scattering contribution. The former is dealt with by a well established procedure of restrained deconvolution in which the low-energy tail of the detector response function is stripped off to leave the spectrum convoluted with a Gaussian of 0.40 au full width at half maximum. Comparisons then must be made with models convoluted with that Gaussian.

Similarly, experience has led to the development of Monte Carlo simulations of the parasitic multiple scattering based on a computer program originally devised by Felsteiner, Pattison and Cooper [22]. Between three and five million incident photons were simulated and this yielded double-scattering corrections equivalent to 15%–22% of the single scattering. Unfortunately the model is developed for samples shaped as discs rather than rectangles, because the circular symmetry is necessary to speed up the inherently slow calculation. Therefore the simulation was made for a disc of area equal to the irradiated portion of the foil; some systematic errors arise in the thicker samples because of this, especially as the mean free path of the incident radiation (~10 mm) is comparable to the sample dimensions.

In the case of the two thinnest samples the smaller computed correction produced symmetric profiles that smoothly approached the free-atom values [18] at the high-momentum extremes ($p_z = \pm 7$ au) as expected. The thicker samples showed poorer symmetry and the requirement to match the free-atom tails was used to scale the multiple-scattering correction for the two thicker samples which differed in width.

The quality of the processed results can be judged from figures 1 and 2. The first shows the reproducibility of two data sets for the same sample by plotting their mutual difference. The peak count in each case was $\simeq 1.5 \times 10^5$, so oscillations within a range of ± 0.015 electrons au^{-1} at the origin merely reflect statistical uncertainties and the data points lie comfortably within this range. Figure 2 shows the left/right asymmetry of the processed profiles of samples S_1, S_2, S_3 and S_4. The fact that asymmetries remain is a reflection of the difficulty in making accurate corrections for multiple scattering in the sources and samples and imperfect charge capture in the detector. All these effects principally degrade the low-energy side (negative p_z) of the Compton line which is

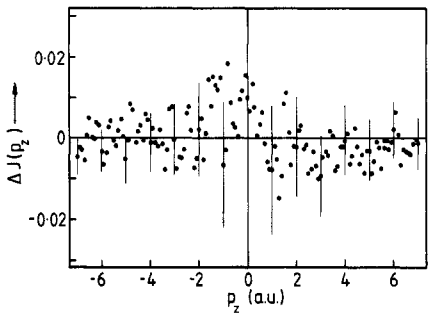

Figure 1. The reproducibility of Compton profiles deduced from data sets measured with different γ-ray sources. The differences between the data sets are plotted and are shown to be within the statistical errors indicated by the vertical lines ($\pm\sigma$).

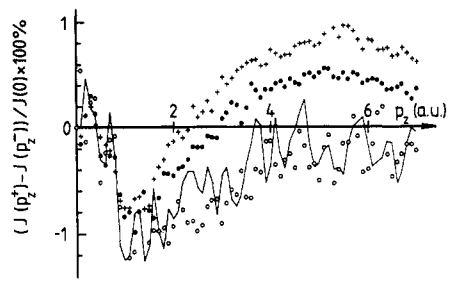

Figure 2. The left/right asymmetry of the processed profiles of samples S_1(+++), S_2(———), S_3(○○○) and S_4(●●●) plotted as a percentage difference of the peak height.

consequently often ignored. In this case the samples S2 and S3 exhibit identical asymmetries within their statistical precision and hence this systematic error will not affect their differences, S3–S2, at either negative or positive momenta. The asymmetries of the S1/S4 pair differ systematically by about two standard deviations because of discrepancies at negative momenta attributable to the multiple-scattering effects; however, inspection of the data reveals that the profiles are mutually consistent at positive momenta and for this reason only the more reliable positive-momenta data are considered for the S1/S4 pair.

4. Interpretation of the results

The formation of difference profiles automatically eliminates the constant contributions from iron, silicon and boron, but the fact that the alloys contain different amounts of nickel and cobalt means that the core contributions do not subtract out: simple difference profiles such as $J^{S1}(p_z) - J^{S4}(p_z)$ would be uninterpretable. Therefore, before differences were formed, a free-atom core profile corresponding to the appropriate Co/Ni composition was calculated from the tables of Biggs, Mendelsohn and Mann [18] for the $1s^2 2s^2 2p^6 3s^2 3p^6$ configuration, convoluted with the resolution function and subtracted from each profile.

This procedure leaves a partial Compton profile, which describes the contributions of the residual 3d (atomic-like) and 4s (free-electron-like) electrons, i.e. $(3d)^{9-p}(4s)^p$ and $(3d)^{10-q}(4s)^q$ components where p and q should correspond to the number of free electrons promoted to the conduction band in cobalt and nickel respectively. The resulting difference profiles $\Delta J_{3d,4s}$ now only show the changes associated with charge transfer between the s and d bands when nickel is substituted for cobalt. These profiles $\Delta J_{3d,4s}(S_3–S_2)$ and $\Delta J_{3d,4s}(S_4–S_1)$ are shown in figures 3 and 4 respectively. The net areas of these curves are not zero because there is an increase of 0.3 in the number of (3d, 4s) electrons per formula unit in the former (figure 3) and 0.55 in the latter (figure 4).

Two observations provide guidance in the analysis of these curves. Firstly the 3d bands will be narrow and reasonably well modelled by atomic wavefunctions which

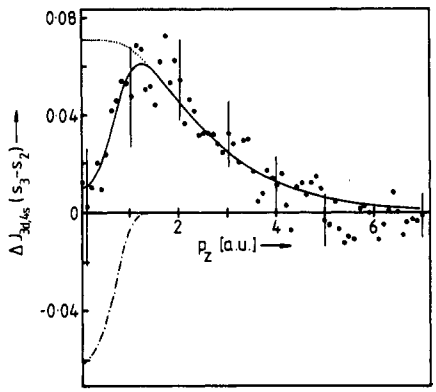

Figure 3. The processed difference Compton profile, $\Delta J_{3d,4s}(S_3-S_2)$. The different core electron contributions in the two samples have been removed and described in the text and these data points (●●●) only reflect the redistribution in the outer electron momentum distribution for the 0.3 electrons/atom. The full curve represents the best fit to the data modelled by a free-atom-like 3d contribution (dotted curve) and a free-electron-like 4s contribution (chain curve). The fact that the latter is negative indicates a charge transfer on alloying from the 4s to the 3d band.

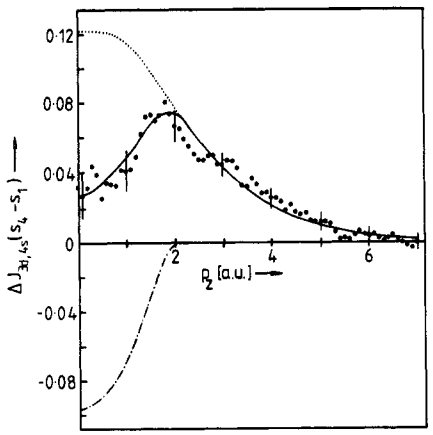

Figure 4. The processed difference curve $\Delta J_{3d,4s}(S_4-S_1)$. The data correspond to a net contribution of 0.55 electrons/atom; symbols etc are as in figure 3.

produce Compton profile contributions that are fairly flat out to about $1\frac{1}{2}$ au and then decrease slowly as shown by the dotted curves in figures 3 and 4. Secondly the Compton profile of a free-electron gas is a truncated parabola, the truncation point, p_F, depending on the free-electron density. In almost all materials, $p_F < 2$ au.

Inspection of the data presented in the figures shows that they can be sensibly fitted by a combination of the broad 3d function and a narrow parabolic one. The fact that the parabola is negative implies that there has been a charge transfer from the 4s conduction band to the 3d band by the number of electrons represented by the parabolic areas, i.e. 0.08 ± 0.02 for $\Delta J_{3d,4s}(S_3-S_2)$ and 0.24 ± 0.01 for $\Delta J_{3d,4s}(S_4-S_1)$. The least-squares fitting allowed the relative number of 3d and 4s electrons to vary subject to the fixed totals of 0.3 and 0.55 electrons for the respective pairs. It produced a good 'chi-squared' fit as is evident from the inspection of the composite curves (full curves in figures 3 and 4) and sensible values of $p_F = 0.9 \pm 0.1$ au and 1.83 ± 0.04 au respectively for the free-electron Fermi momenta. Hence, one can conclude that the replacement of cobalt by nickel is associated with an additional charge transfer from the 4s conduction band to the 3d band. This charge transfer could explain the disappearance of the magnetic moment of nickel in amorphous alloys.

It is also generally known that disorder enhances localisation of electron density, $\rho(r)$ in the vicinity of atoms. Thus the Compton profiles of conduction electrons may contain more higher-momenta components, and this trend will increase with the degree of disorder. Such a mechanism could qualitatively explain the pronounced difference in the Fermi cut-off momenta (0.9 for S2/S3 and 1.8 for S1/S4 pairs). This point, however,

needs to be studied in a separate experiment in which the ambiguities connected with the geometry of scattering (mainly with the multiple-scattering correction problem) are removed.

In conclusion, these results provide evidence for charge transfer in Co/Ni amorphous alloys and illustrate the value of Compton scattering studies of disordered systems, a class of materials that has been largely neglected in previous work.

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