# RESEARCH GROUP DATA ARCHIVE

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# Overview

This archive contains data collected over the time that Collins did research at WSU between 1985 and the present. This research was supported externally by the National Science Foundation under a succession of nine multi-year single-investigator grant awards to WSU from the Metals Program (later, MMN Program) of the Division of Materials Research. The grants were:

1987-90  NSF grant DMR 86-19688, Metals Program, *Point Defects in Metals Studied by Hyperfine Interactions*. ($240,000).

1990-93  NSF grant DMR 90-14163, Metals Program, *Atomic Structure and Defects in Metals and Alloys Studied by Hyperfine Interactions*. ($275,000).

1993-96  NSF grant DMR 93-13702, Metals Program, *Point Defects in Intermetallic Compounds*. ($325,000).

1996-99  NSF grant DMR 96-12306, Metals Program, *Defects and Diffusion in Intermetallic Compounds*. ($356,320).

2001-04  NSF grant DMR 00-91681, Metals Program, *Studies of Point Defects in Intermetallics using PAC* ($419,556).

2005-09  NSF grant DMR 05-04843, Metals Program, *Lattice Location of Solutes and Diffusion in Intermetallics*. ($500,000).

2009-13  NSF grant DMR 09-04096, Metals Program, *Diffusion in Rare-Earth Binary and Ternary Intermetallics Studied using PAC* ($420,000).

2014-17  NSF grant DMR 14-10159, Metals and Metallic Nanostructures, *Diffusion and solute-solute interactions in intermetallic compounds*, ($360,000).

2018-21  NSF grant DMR 18-09531, Metals and Metallic Nanostructures, *Partition of solute atoms among sublattices in intermetallic compounds*,. ($408,278)

Links to further information about grant activities can be found under Collins's ORCID URL https://orcid.org/0000-0002-7334-9831, including links to NSF's non-technical descriptions of the projects.

# Structure of the Archive

There are two parallel archives, one of raw spectral DATA and the other of spectral ANALYSIS. There is a small number of other spectra, such as of positron lifetimes, x-ray diffractograms,

**"DATA"** contains raw data in the form of spectra measured as a function of delayed coincidence time (PAC) or velocity shift (Mössbauer effect) due to source motion. There is a small number of other kinds of spectra, including positron lifetimes, x-ray diffractograms, etc. This archive is mostly organized in folders by the principal solid-state phase under study, such as "Ni" for nickel metal, or "Al3Ni" for the intermetallic compound. All samples of "Al3Ni" studied will have raw data in the same folder. Each data file is identified by a date-code of the day in which the spectrum was saved. Thus, for example, 070418q.raw identifies a spectrum saved on April 18, 2007. For PAC spectra, there were two spectrometers, PAC1 and PAC2. Files saved on PAC1 had letters "a", "b", "c"... appended to identify if it was the first, second... file saved on that day. Similarly, files saved on PAC2 were tagged with letters "p", "q", "r"... Thus, file 070418q.raw was the second file saved on PAC2 on April 18, 2007. Data files originated on a DEC 3000 Alpha workstation, running under the time-sharing operating system VMS. VMS automatically appends version numbers at the ends of file extension names so that, for example, 070418p.raw;3 is version 3 of file 070418p.raw. These version numbers have not been removed. It is believed that all, or nearly all, files in the DATA archive are alphanumeric.

**"ANALYSIS"** contains scans of results of spectral fits, mostly with images of the fitted spectra and parameters fitted by the least mean-squares method, often with values of the reduced Chi2 for the fit that, for good data and an appropriate fitting function, should be a number close to 1.0. All fitting programs were written by Collins. Results of the fits were scanned, with separate folders for each phase, such as "Al3Ni", and separate pdf files for each sample studied. For example, folder "Al3Ni" has five subfolders: "Al3Ni-23%Ni.pdf", "Al3Ni-23.15%Ni.pdf", "Al3Ni-25.36%Ni.pdf", etc. Generally, each sample was studied as a function of temperature, or after a series of isochronal annealings, with results of all runs for a sample contained within the same pdf file.

**Unique sample identifications**. Samples were nearly all made by arc-melting high-purity metals together with $^{111}$In activity under argon. Each sample is identified by two initials of the person who melted the sample, for example, SJ022 was the 22$^{nd}$ sample melted by Slade Jokela, on or about October 1, 2007. A list of preparers is given below.


# Experimental Methods

## 1. Perturbed angular correlation of gamma rays (PAC).

The data archive consists primarily of time-series spectra obtained by the *Perturbed Angular Correlation* (PAC) method, a nuclear hyperfine spectroscopy similar to nuclear magnetic resonance or Mössbauer effect that can provide atom-level resolution of the locations of radioactive probe atoms in solids through interactions between the nuclear moments of the probe atoms and internal fields in solids. In most experiments, it was through the interaction of the quadrupole moment of an excited nuclear state in the local electric field-gradient (EFG) at the probe atom's site. Almost all measurements were carried out using the $^{111}$In probe, which decays with a mean life of 4.0 days to the second excited state of $^{111}$Cd, which in turn decays to the first excited state and then the ground state. The first excited state, at 247 keV, the so-called

"PAC level", has a mean-life of 120 ns, long enough for the quadrupole moment of the state to precess through a few revolutions in the torque exerted on it by the EFG.

**RAW data files**. The PAC spectrometers consist of four scintillation detectors arranged in a plane at 90-degree intervals around the sample and numbered 1-4 in sequence. Counts from either detectors 1 or 2 were used to trigger or start the time-to-amplitude converter (TAC) and counts from detectors 3 or 4 to stop the TAC. Four coincidence spectra were thus accumulated between detector pairs 1-3, 1-4, 2-3 and 2-4, with relative angles of 180°, 90°, 90°, 180°. The spectra were stored in sequence in raw-data ascii files in integer format with extension names ".raw". There were two four-counter spectrometers, named PAC1 and PAC2. Since some time in the 1990's, all four subspectra were combined in sequence in one large file of four 2048 channel spectra, or 8192 channels, eight channels to one line, in integer format.

**Double-sided spectra**. In early years, stop counts were delayed by or order 10-50 ns, putting "time zero" out about 10-50 channels (the typical delay time per channel was about 0.95 ns). Later, using digital delay generators from EG&G Ortec, the time scan of a spectrum was set to ~2 microseconds over 2048 channels, with "time zero" positioned close to channel 1024, the middle of the spectrum. Consider detector pair 1-3. Energies were gated (accepted) if the start gamma was detected in det-1 and the stop in det-3 (the normal time sequence) or if the start gamma was detected in det-3 and the stop in det-1 (the inverse time sequence). By routing both conditions into the same coincidence spectrum, one obtains a "double-sided" spectrum, with equivalent data at relative negative-time "mirroring" the normal data at positive relative time. A cost of the method is to double the accidental backgrounds in the spectrum. Thus, many spectra in later years have "time-zero" close to channel 1024, with equivalent data at positive and negative relative times.

**REDUCED data files**. A preliminary fitting program, named PAC or PACQ, was used to read in a "raw" file and then to fit and subtract accidental backgrounds in each of the four subspectra. This gives four background-subtracted spectra $W_{13}$, $W_{14}$, $W_{23}$, and $W_{24}$. After that, the two spectra at each angle were geometrically averaged; that is

$$W(\pi,t) = \sqrt{W_{13}(t)W_{24}(t)}, \text{ and } W(\pi/2,t) = \sqrt{W_{14}(t)W_{23}(t)}, \tag{1}$$

and then algebraically combined to yield an experimental perturbation function $G_2(t)$,

$$G_2(t) = \frac{2}{A_2\gamma_a}\frac{W(\pi,t) - W(\pi/2,t)}{W(\pi,t) + 2W(\pi/2,t)}, \tag{2}$$

called the "reduced data". In eq. 2, A2 is the anisotropy of the angular correlation, -0.175 for the PAC level of $^{111}$Cd, and $\gamma_a$ is an angular attenuation coefficient arising from the finite solid angles of the detectors, typically ~ 0.7. The above method of combining individual spectra largely leads to cancellation of effects owing to different detector distances from the radioactive source, differing detector efficiencies, and energy window settings. Uncertainties in the values of $G_2(t)$ were obtained from counting statistics.

The main output of this preliminary fitting program is an ascii file in G or E format, with values of $G_2(t)$ followed by errors, two channels on a line, with filename extension ".red". One could also output a file ".org" in a format designed for producing publication quality figures using the scientific graphics program "Origin". All .raw, .red, .org, etc. files are in the DATA archive.

**Generating fourier frequency spectra from the measured time series**. ".red" files could be imput into program **FFT**, to produce a fourier frequency spectrum of the reduced data file. There was provision to generate an output numeric ascii file ".fft" for production of figures that can be found in the **DATA** archive. For double-sided spectra, window carpentry was used such as by multiplying the spectum by a carpentry function such as a triangle (Bartlett window) or cosine function (Tukey-Hanning window) both to reduce the statistical influence of data far from time-zero and to reduce "side lobes" or "satellite lobes" near intense fourier peaks.

## FITTING PAC SPECTRA.

Reduced data ".red" files were read into and fitted with one of many time-series curve-fitting programs, with names like **PACR01** or **PACS20**, in which the numeric identifier refers to various different function fitting subroutines that are compiled with the main program. Outputs of the fitting program include printouts of images of the fitted spectra as well as the fitting parameters and reduced Chi2 goodness-of-fit parameter. Most fitting functions were superpositions of up to seven spin-5/2 quadrupolar perturbation functions, which have the general form

$$G_2(t) = a_0 + a_1 \cos \omega_1 t + a_2 \cos \omega_2 t + a_3 \cos \omega_3 t, \tag{3}$$

in which, for a single signal, the amplitudes $a_0$-$a_3$ sum to 1.0, $\omega_3 = \omega_1 + \omega_2$ and $1 \le \omega_2/\omega_1 \le 2$. The fits give information about the electric-field gradient tensor at the nuclear site. Because the tensor is symmetric and traceless, there are two independent variables that can be fitted, which have been taken in all our work to be the fundamental measured frequency $\omega_1$ and the asymmetry parameter of the efg tensor, $\eta = \left|(V_{xx} - V_{yy})/V_{zz}\right|$, in which $V_{zz}$ is the component of the efg tensor having largest magnitude. Thus, $0 \le \eta \le 1$. For a random, polycrystalline sample, and assuming that there is a 3- 4- or 6-fold axis of symmetry about the principal axis of the efg tensor (so-called axial symmetry), $\omega_1 : \omega_2 : \omega_3 = 1 : 2 : 3$, and $a_0 : a_1 : a_2 : a_3 = 7/35 : 13/35 : 10/35 : 5/35$. For axial symmetry, $\omega_1 \equiv \omega_0 = \frac{3\pi}{10} eQV_{zz}/h$. The relationships between the frequencies $\omega_1 - \omega_3$ and $\eta$ are complex. The fitting routines used the ratio $\omega_2/\omega_1$ in a convenient approximant for the asymmetry parameter equal to $\eta' \equiv 2 - \omega_2/\omega_1$, and then a look-up table was used to find the corresponding value of the true asymmetry parameter $\eta$ from fitted values of $\eta'$. Very crudely, $\eta' \cong \eta$ except when they are both close to zero.

Additional fitting parameters were used for line broadening. For *inhomogeneous* line broadening, it was assumed that each frequency component of perturbation function gets damped out in the same number of "wiggles". Thus, eq. 3 generalizes to

$$
\begin{aligned}
G_2(t) = a_0 &+ a_1 \cos\omega_1 t \exp(-(\sigma\omega_1 t)^p) + \\
&+ a_2 \cos\omega_2 t \exp(-(\sigma\omega_2 t)^p) + , \\
&+ a_3 \cos\omega_3 t \exp(-(\sigma\omega_3 t)^p)
\end{aligned}
\tag{4}
$$

in which $\sigma$ is the broadening parameter and $p$ is the power of the damping ($p=1$ for exponential damping, $p=2$ for gaussian). Frequently there were more than one function fitted, so that the composite perturbation function was taken to be a sum of functions such as in eq. 4 multiplied by a site-fraction $f$.

Results of fits and of fourier transforms were printed out. They were recently scanned and the pdf files generated are given in the **ANALYSIS** archive. In addition, some worksheets in the files were also scanned and included.

**2. Mössbauer spectroscopy.** To be added later.

**3. Other spectra.** To be added later, such as x-ray diffractograms, positron lifetime spectra.

## Additional information about the archives

There are folders for each phase studied, e.g. Ga7Pd3 or GdAl2, including in each folder results for multiple samples of that phase. Files of raw numerical data in ascii text format with various filename extensions given below. Filenames are unique identifiers for a saved spectrum. They include a date code identifying the day on which the spectrum was saved followed by a letter code identifying whether the spectrum was measured on spectrometer PAC1 (letter codes are sequential during the day, starting with "a") or PAC2 (letter codes start with "p"). For example, 070817q is the filename for the second spectrum saved on PAC2 on Aug 17 2007.

A. <u>Data Archive</u>. File types.

> .raw — PAC "raw data", the distributions of time intervals between arrivals of gamma-1 and gamma-2, signaling formation and decay of the intermediate PAC level. Data are numbers of counts in four subspectra of 1024 or 2048 channels strung together one after the other, ascii in integer format. A header line gives information about the spectrum, beginning with the date on which it was saved (e.g. 070914= Sept 14 2007), the metal phase and composition, temperature of measurement ("Tm", RT= room temp~ 20 C), and sample identifier (e.g., JB073= sample 73 prepared by John Bevington). The four subspectra are time-delayed coincidence spectra

> .red — PAC "reduced data"; output of a preliminary fitting program that simply fits and subtracts constant backgrounds from accidental coincidences, leaving exponential decays. Ascii file in G or E format.

> .fft — Output file of frequency spectrum generated using the fast fourier transform. Ascii file in F format.

> .org — Files for production of publication figures using Origin. Ascii file in G or E format.

B. <u>Analysis Archive</u>. Scans of fits of time-series spectra, partial results of preliminary fits of PAC spectra (on one page), and fourier frequency transforms, all in pdf format. There is a separate file for each <u>sample</u>, contained in a common folder for each <u>phase</u>. Thus, for example, a folder for <u>Al2Gd</u> contains files for different samples, including <u>Al2Gd-31.38%Gd.pdf</u> and <u>Al2Gd-35%Gd.pdf</u>. Each file stands for one sample and has a cover page listing phase, composition, sample identifier, and date code for one of the spectra included. For example,

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Al3Hf
27.92%(27.50-29.01) Hf
SJ022
20071001

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The composition is nominally obtained from masses of the element foils melted together, but there is generally a small amount of mass loss during a melt, either due to evaporation or some other loss of a small amount of the sample. To take into account the mass loss, the range of composition was calculated assuming that the mass loss was all from (in the example) Al or Hf. Since the atomic mass of Hf is so much greater than that of Al, the range is not symmetrical about the nominal composition.

The sample identifier gives the initials of the researcher who prepared the sample by arc-melting. In the example, this was the 22nd sample created by SJ= Slade Jokela. Many measurements may have been made on one sample, up to about ten. The date code gives the date for one of the measurements. Combining the date code and sample identifier, one can look at details of the sample creation in sample preparation notebooks, kept in room 755, and also for notes taken during the measurements in the run books, kept in room 634.

**Other information available supporting the archive**

There are two sets of laboratory notebooks with additional information for PAC measurements.

1. Sample Preparation Notebooks. Housed in Webster Hall room 755, where nearly all sample preparations were made. They contain information about masses of pure metals that were subsequently melted, qualitative comments about the quality of the melts (e.g., did the sample form up into a nice sphere that solidified, or not?), measurements of sample mass before and after melting. Generally there was a small mass loss during melting, of order 1 %, attributed to evaporation of one metal or the other of an alloy, or ejection of a small fragment of one metal. The balance has a precision of 10 micrograms. Uncertainty in the final composition of an alloy sample was determined by conservatively assuming that mass loss was entirely from one host metal component or the other. These calculations are in the notebooks. Occasionally, sample masses were remeasured after measurements at high temperature, sometimes showing evaporation of large fractions of the sample mass.

2. Experiment run books. Housed in the measurement lab, Webster room 634. There are separate run books for setups PAC1, PAC2 and the Moessbauer spectrometers and give details about the individual runs of samples.

3. Other laboratory notebooks. There are also run books for the DEC 3000 Alpha workstation, the multinode Dell workstation used for WIEN2k electronic structure calculations, the turbopumps, etc.

## List of sample preparers

Below is a table of group participants who prepared samples, including their two-initial identifiers, names, periods of association with the group, and project descriptions.

| Initial | Preparator | When in group | Research Project |
|---|---|---|---|
| AB | Andrew Bleasdale | Jan 14 – May 17 | Miedema model for site preferences of solutes in compounds |
| AD | Ashley Dorwart | May 07 - Aug 07 | Lattice locations of indium in Gd-Al alloys |
| AF | Aurélie Favrot | Jun 03 - Sep 03 | Site preference and diffusion of solutes in compounds |
| AJ | Andrew Janssen | Sep 98-Dec 98 | Point defects in FePd (Mössbauer) |
| AL | Arriety Lowell | Jan 06- May 07 | Site preferences in rare-earth aluminides of C15 structure |
| BB | Bin Bai | May 95-Sep 97 | Equilibrium defects in NiAl (PAC) |
| BM | Bruce H. Meeves | May 92- Dec 93 | Formation of FeCo and $Ni_3Fe$ by mechanical alloying |
| BN | Ben Norman | Jan 07- May 08 | Solute atoms in "mirror" phases (WSU honors thesis, Oct 07) |
| BW | Bonner C. Walsh | Aug 01- May 02 | Site selection of solutes in compounds |
| DB | Debashis Banerjee | Nov 15 – Jan 16 | Solute-solute interactions in intermetallic compounds |
| DS | Denys Solodovnikov | Mar 03 -Dec 03 | Diffusion in several rare-earth indide compounds |
| EN | Egbert Rein Nieuwenhuis | Sep 03- Jun 04 | Diffusion in $Ga_7Pd_3$; Polymorphic transformation in In2La |
| FS | Farida Selim | Nov 05 – May 07 | Site-preferences and atom movement in compounds (PAC) |
| GK | Gil-Hong Kim | Jan 90- Jul 90 | Defects in annealed and quenched TiAl |
| GM | Gregeory McGhee | May 88-May 89 | Defects in hcp Co; non-observation of hydrogen in Au or Cu |
| HJ | Hwa-Jae Jang | Jan 87- Jun 88 | Hydrogen decoration of vacancies in Pt |
| HN | Harmen Thys Nieuwenhuis | Jan 98 - May 98 | Vacancy motion in PdIn |
| JA | Justin Ahn, Pullman HS | Jun 07-May 08 | Diffusion in intermetallic compounds including $In_3Nd$ |
| JB | John P. Bevington | Aug 08-May 11 | PAC and DFT studies of $Al_3Ni$, $Al_3Ti$, $Al_3Zr$, and $In_3R$ phases |
| JF | Jiawen Fan | May 89-May 92 | Thermal defects in quenched NiAl and CoAl (PAC) |
| JM | Jesse Miller | Feb 11 – Apr 12 | Temperature dependence of hyperfine magnetic field in Ni |
| JM | Justine Minish | Jun 10 - Aug 10 | Diffusion in pseudo-binary $La(In,Sn)_3$ alloys |
| JS | John Sy | May 91-Jun 92 | Martensitic phase transformation in NiTi |
| JW | Jipeng Wang | Sep 03- May 04 | Diffusion in $LaSn_3$ |
| KB | Kirk Burris | May 90-May 91 | Defects in alloys; nanoclusters |
| KD | Kenneth Dorrance | Jan 10 – Dec 11 | Wigner-Seitz cells: calculating volumes and contact areas |
| KE | Kyle Elsasser | Aug 18- | Studies of solutes in intermetallics |
| KK | Krystal Kasal | Jun 14- Jun 15 | Investigations of ternary alloys using PAC |
| KS | Kyle Slinker, Pullman HS | Jun 05-Aug 06 | Analytic calculation of properties of Wigner-Seitz cells |
| KZ | Khushairi Zainun | May 88-May 89 | Laser surface-melted metals |
| LA | Lee Aspitarte | May 10 – Aug 11 | Polymorphic and peritectic phase transformations in $In_3Zr$ |
| LK | Li Kang | Nov 03-May 04 | Diffusion in $CeIn_3$ |
| LP | Luke S.-J. Peng | May 98 – Feb 99 | Point defects in FeAl and NiAl; phase embryos (PAC) |
| LP | Shing-Jen (Luke) Peng | May 93-May 98 | Defects in annealed and milled FeAl and FeRh (Mössbauer) |
| LW | Lai Wang | Jan 05- May 05 | Analytic calculation of Wigner-Seitz volumes in compounds |
| ML | Megan Lockwood | May 08 - Aug 08 | Jump frequencies of Cd tracer atoms in tin intermetallics |
| MP | Matthew Petersen (UI) | May 99-Aug 99 | Point defects in quenched and annealed FePd (Mössbauer) |
| MW | Mingzhong Wei | May 95 -May 98 | Point defects in FeAl studied by PAC |
| MZ | Matthew O. Zacate | Mar 99 - May 03 | Site-preferences, quadrupolar diffusional relaxation (PAC) |
| PH | Phillip Himmer | May 88-Aug 89 | Point defects in oxides & palladium |

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|---|---|---|---|
| PP | Phillip Peterman | Jan 05- May 05 | Numerical calculation of Wigner-Seitz cell volumes |
| PS | Prastuti Singh, Pullman HS | Jun 09-May 10 | Diffusion in $CoGa_3$ (*Intel Science Talent Search* winner) |
| PS | Praveen Sinha | May 90-Jul 95 | Defects in quenched and mechanically milled PdIn (PAC) |
| QW | Qiaoming Wang | Jan 11– May 12 | Site preferences and diffusion in rare-earth palladides |
| RH | Ryan Harrison | Summer 2013 | Miedema model for site preferences of solutes in compounds |
| RM | Ryan Murray | Sep 14-May 17 | Solute-solute interactions in intermetallic compounds |
| RN | Randal Newhouse | Dec 07-Oct 12 | Diffusion in ordered compounds and pseudo-binary alloys |
| SC | Samantha Cawthorne | May 09 - Aug 09 | Diffusion in $Al_4Sr$ and $Ga_4Sr$ |
| SI | Stacy Irwin | May 89-Dec 89 | Point defects in rhodium |
| SJ | Slade Jokela | May 01-Aug 01 | Solutes in intermetallic compounds |
| SL | Stephanie Lage | May 06- May 07 | Dynamics of tracer atoms in intermetallic phases $Al_{11}R_3$ |
| SS | Steven L. Shropshire | Dec 88-Aug 91 | Studies of defects and defect interactions in metals (PAC) |
| WO | Windy Olsen | Nov 17- | Studies of solutes in intermetallics |
| XJ | Xia (Sean) Jiang | Jan 07- May 08 | Jump frequencies of In/Cd probe atoms in $L1_2$ gallides |
| XW | Xiao Wang | Jan 06- May 07 | Defects in II-VI semiconductors such as ZnS using PAC |
| XY | Xiangyu (Desmond) Yin | Oct 09– May 11 | PAC studies gallium and eutectic gallium alloys |