Vibrational properties of Pu and Ga in a Pu-Ga alloy from neutron-resonance Doppler spectroscopy

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We have determined some of the phonon spectral parameters for Pu and Ga in the ''stabilized'' δ phase (fcc) of the Pu-3.6 at. % Ga alloy by measuring the Doppler broadening of neutron resonances as a function of temperature. We find the mean phonon energy (first moment of the phonon spectrum) of Pu to be $\langle h\nu \rangle = 8.22 \pm 0.12$ meV and the second moment to be $\langle (h\nu)^2 \rangle = (7.2 \pm 0.3) \times 10^{-5}$ eV^2. These moments and the value of the (-1)st moment determined from Debye-Waller factors from neutron powder diffraction are consistent with a Debye model with a Debye temperature of 127.2 ± 1.7 K. For Ga in the Pu-Ga alloy, $\langle h\nu \rangle = 16.3 \pm 1.4$ meV, which is slightly larger than the $m^{1/2}$-weighted value of 15.3 meV expected from the value for Pu (however, the measured value cannot be distinguished from the latter value within experimental error). These results show that Pu-3.6 at. % Ga behaves very much like a Debye solid at ambient pressures and low temperature and that the Ga impurity experiences approximately the same (or a slightly stiffer) force field compared with the Pu it replaces. [S0163-1829(98)04538-X]

I. INTRODUCTION

Plutonium sits at a boundary in the actinide series that separates $5f$ electron localization and itinerancy. To its left in the periodic table, the f electrons are delocalized and contribute to the bonding; to its right, the electrons are localized and do not. Among other things, this results in an extremely rich structural morphology and instability which is displayed in the existence of six allotropic phases before it melts at 914 K as it is heated at ambient pressure.[1] Therefore it is not surprising that neutron powder diffraction studies across all of its phases indicate the presence of large amounts of diffuse scattering or that the atomic displacement parameters, derived from these studies, show the steep temperature dependence suggestive of low Debye temperatures.[2]

The face centered cubic δ phase of Pu is perhaps the most interesting of these because the partial localization of the $5f$ electrons leads to a 17% increase in volume compared with the monoclinic α phase. This also leads to a negative coefficient of thermal expansion. Unfortunately, the partial localization also means that it is one of the least well understood phases in terms of its electronic structure. The phase is usually stable from 583 to 725 K, but the stability of this phase can be extended to lower temperatures by the addition of δ-phase stabilizers which enter the lattice substitutionally.[3,4] Ga is the most commonly used stabilizer and is soluble to about 9 at. %. At concentrations above about 3 at. %, the δ phase is stable to below 10 K. The stabilized δ phase exhibits a number of unusual properties. (1) Cox *et al.*[5] have reported an x-ray absorption fine structure (XAFS) study of the structure of 3.3 at. % Ga doped plutonium alloy. The XAFS studies at the Ga K edge showed that its nearest neighbors are well ordered (with a sharp peak), as are atoms in the second and third coordination shells. The Pu $L_{\rm III}$-edge data showed that the plutonium environment is substantially less well ordered, with the peaks from the second and third coordination shells completely absent. (2) δ-Pu shows evidence of having a soft-mode instability and has the most anisotropic shear wave elastic constants known for any fcc metal [C_{44} is approximately 7 times greater than $C^* = (C_{11} - C_{22})/2$], even though its $5f$ electrons are mostly localized.[6]

An understanding of the vibrational properties of fcc δ-phase Pu alloys is important to the understanding of the behavior of Pu and for the mechanism for δ-phase stabilization. At present what is known about the vibrational properties comes from studies of the temperature dependence of the Debye-Waller factors from neutron powder diffraction studies.[2] These results showed that stabilized δ-phase Pu has an extremely low Debye temperature of 132 K, but the Debye-Waller factors for Pu and Ga had to be constrained to be the same. Understanding the differences in vibrational behavior between Pu and Ga should lead to an understanding of the different force fields these atoms experience. This should be important to understanding the electronic structure of the alloy and to an understanding of the stabilization mechanism.

In this article, we use the Doppler broadening of the individual resonances in the neutron cross sections of these elements to obtain information about the vibrational properties of Pu and Ga, separately, in a Pu-3.6 at. % Ga alloy. Neutron resonance Doppler broadening techniques were first introduced by Jackson and Lynn[7] to compare the width of the 6.67 eV ^{238}U resonances in metallic U and in U_3O_8. More recently, Meister *et al.*[8] have extended this work to include other resonances in the study of U and UO_2. In order to test the technique for the reliability of the derived Debye temperatures, we have been comparing measured values for various metals (such as W and Ta) with those obtained from low temperature heat capacity measurements and, in general, find good agreement.[9] This technique also has been used in the study of vibrational energy in the high-T_c cuprate superconductors. Ikeda *et al.* reported surprisingly high values of the Debye temperature for the Cu and O vibrations in both the $YBa_2Cu_3O_{6+\delta}$ and $La_{2-x}Sr_xCuO_4$ families of

superconductors.[10] Unfortunately, these did not agree well with much lower (and more reasonable) values of the Debye-Waller temperatures derived from neutron powder diffraction.[11,12] Mook *et al.*[13] used these techniques to study the CuO_2 phonons in single crystals of the $Bi_2Sr_2CaCu_2O_8$ superconductor and observed a sharp decrease of the phonon energy resulting in a steeper temperature dependence of the in-plane phonons in the superconducting state. We studied the $La_{2-x}Ba_xCuO_4$ system[14] which is superconducting over the doping range $0.5 \leqslant x \leqslant 2.2$, except at compositions around $x=0.125$ (the so-called $\frac{1}{8}$ doping anomaly).[15] This sensitive dependence of superconductivity allowed us to study the vibrational behavior of superconducting and nonsuperconducting samples that differed only slightly in composition. We found that the low-temperature mean phonon energy for the La ions was nearly twice as large for $La_{1.85}Ba_{0.15}CuO_4$ (superconducting) as it was for $La_{1.875}Ba_{0.125}CuO_4$ or La_2CuO_4 (both nonsuperconducting). The stiffening of the lattice in the superconducting state observed by Mook *et al.*[13] and by us[14] has also been observed for single crystals of $RBa_2Cu_3O_{6+\delta}$ ($R=$ Y or Er) in ion-channeling experiments along the crystalline c axis.[16] The work reported here is different from the other work in that the objective is to explore how the force fields change when an impurity atom is inserted substitutionally into a host crystal.

II. GENERAL THEORY

The slow neutron cross sections of most heavy nuclides have resonances in their energy dependence that are narrow enough to be significantly Doppler broadened. The detailed nature of the Doppler broadening depends on the environment in which the nucleus is embedded, i.e., the solid, liquid, or gaseous state and its temperature. Information on the nuclear environment can therefore be extracted by detailed measurement of the form of the neutron cross section in the resonance region.

The basic papers are those by Bethe[17,18] on Doppler broadening in a gaseous medium, and Lamb[19] on the basic formalism for crystals. The work of the latter has been developed[20] to produce expansions for the Doppler broadening function that depend on the moments of the phonon spectrum of the crystal (or, in a multiatomic compound or alloy, the fraction of the spectrum that resides on the nucleus carrying the resonance). The effective cross section that can be measured for a nucleus in its material environment is

$$\sigma_{\mathrm{eff},t}(E_n)=\int dE' S(E')\sigma_t(E_n-E'), \tag{1}$$

where σ_t is the true neutron cross section (for a free, stationary nucleus) and $S(E')$ is an energy-transfer function (the Doppler broadening function) governing the transfer of energy with the environment of the nucleus in the neutron absorption process. At energies close to a resonance in the cross section the form of σ_t is usually well approximated by the single-level Breit-Wigner formula

$$\sigma_t(E)=\pi\lambda\!\!\!^{-2} f_i s_J \Gamma_n \Gamma_r / [(E-E_\lambda)^2 + 1/4\Gamma^2], \tag{2}$$

where $2\pi\lambda\!\!\!^{-}$ is the De Broglie wavelength at energy E, f_i is the fractional isotopic abundance, s_J is the probability of the spins of the nuclear system combining to form the total angular momentum J of the resonance state, Γ_n is the neutron width, Γ_r is the reaction width (in the slow neutron resonances of heavy nuclei this usually comprises the radiation width Γ_γ and the fission width Γ_f), E_λ is the resonance energy, and Γ is the total width. A useful and accurate expression for this energy-transfer function is

$$S(E')=\frac{1}{\Delta\pi^{1/2}}\exp[-(E'-R)^2/\Delta^2] \times\left[1+\sum_{n=3}^{\infty} a_n H_n[(E'-R)/\Delta]\right], \tag{3}$$

where R is the recoil energy that would be carried off by the compound nucleus after absorption of the neutron by a free, stationary target nucleus, the H_n are the Hermite polynomials, and the ''Doppler width'' for a crystalline sample is

$$\Delta=[2R\langle h\nu\rangle_T]^{1/2}, \tag{4}$$

$$\langle h\nu\rangle_T=\int d\nu h\nu g(\nu)\coth(h\nu/2kT), \tag{5}$$

$g(\nu)$ is the spectrum of phonon frequencies ν carried by the crystal, k is Boltzmann's constant, and T the sample temperature. The coefficients a_n are functions of the simple even moments of the phonon spectrum, the odd moments with the additional Boltzmann weighting factor [as in Eq. (5)], and the classical recoil energy resulting from absorption of the neutron by the stationary target nucleus. The first two terms within the summation of Eq. (3) have the coefficients

$$a_3=\langle(h\nu)^2\rangle/12\Delta\langle h\nu\rangle_T, \tag{6}$$

$$a_4=\langle(h\nu)^3\rangle_T/96R\langle h\nu\rangle_T^2, \tag{7}$$

The principal parameter that can be determined by measurements of the effective cross section is Δ, the Doppler width, and hence the first Boltzmann-weighted moment $\langle h\nu\rangle_T$. At very low temperatures this becomes simply the mean energy of the phonon spectrum. Also at low temperatures the additional terms with coefficients a_3, a_4, marking departures in skewness and kurtosis from the simple Gaussian, are significant for low-energy resonances and hence can give information on the second and third moments of the phonon spectrum. Such phonon information, specific to the resonant atomic type, is valuable to the understanding of the vibrational properties of materials.

At high temperatures (generally speaking, $\geqslant$75 K) the ''moment'' $\langle h\nu\rangle_T$ approximates to the temperature

$$\langle h\nu\rangle_T=2kT+\langle(h\nu)^2\rangle/6kT-\cdots \tag{8}$$

while the coefficients a_n of the terms beyond the simple Gaussian of Eq. (3) become very small. Equation (3) is then approximated by the classical gas formula of Bethe.[17,18]

In the work described below the effective total cross section is measured in the transmission mode. The count-rate yield at the detector is a fraction of the open beam count-rate C_o, which includes a background fraction $B(E)$. The observed count-rate is spread in time by the resolution function Z, giving a final observed count-rate

$$C(E)=\int dE'Z(E,E')C_o(E')\{[1-B(E')]\times\exp[-n\sigma_{\mathrm{eff},t}(E')]+B(E')\},\quad(9)$$

where n is the thickness, expressed in atoms per unit area perpendicular to the neutron beam of the transmitting material.

III. EXPERIMENTAL PROCEDURES

Neutron energies are measured by the time-of-flight method. The pulsed source used in our measurements is the Manuel Lujan Jr. Neutron Scattering Center (MLNSC) target of the 800 MeV proton linear accelerator at the Los Alamos Neutron Science Center (LANSCE). The protons from this accelerator are compressed into triangular pulses of 125 ns duration (half width at full maximum) by a storage ring and delivered to the target at a rate of 20 Hz. The MLNSC target comprises two separate tungsten cylinders aligned along the proton beam direction surrounded by a complex system of moderators and reflecting blocks of beryllium and nickel. High-energy neutrons (several MeV) are produced by the spallation reaction of the 800 MeV protons with the tungsten nuclei. Many of these are moderated to thermal and epithermal energies. The reflectors serve to increase intensity in the moderated pulse by returning otherwise lost neutrons to the moderators. Flight path 5 facing onto this target system was used for our measurements. The moderator material facing into this flight path is water. Flight path 5 runs at an angle of 15° with respect to the perpendicular to the moderator face.

The neutron beam is collimated down to about 1 cm diameter at about 8 m from the target where the experimental samples are placed, beyond which it diverges until it reaches the neutron detector situated at approximately 58 m. The active material of the detector is ^{6}Li loaded glass scintillator. Seven photomultiplier tube modules, each with a 12.5 cm diameter scintillator, comprised the detector system. Because the MLNSC source is so intense (60 μA of proton current is normally delivered to the target), neutron detection events are very closely spaced in time. Therefore most of the measurements were made in current mode using a transient recorder. The standard XSYS data acquisition and analysis computer system at the beam line was used to record the data. The current mode of operation brings with it a set of complications relating to resolution (these are detailed below). For this reason a set of additional measurements were made in which discrete events were recorded (counting mode data). To reduce the density of detection events sufficiently to allow this, the seven large PMT modules were replaced by a single module with a 5 cm diameter scintillator.

Ideally, samples are in the form of discs and are placed in the neutron beam perpendicular to its direction. Disc thicknesses (usually expressed as atoms/b) are chosen according to the strength of the resonance that is of interest. If possible, a range of thicknesses is used based roughly on the conditions $0.1<n\sigma_0<10$, where σ_0 is the peak effective cross section of the resonance. The principal sample material was a plutonium-gallium alloy containing 3.6 at. % of gallium. This fraction of gallium stabilizes the alloy into the plutonium δ phase down to temperatures below 10 K. The isotopic content of the plutonium is immaterial for its material physics properties (excepting long-term radiation damage), but is of great significance for analysis of the neutron resonance data. The assay of the plutonium by coulometry gives the isotopic data shown in Table I. All samples were rolled and then cut into disks approximately 2.54 cm in diameter, and finally annealed. The dimensions of the samples are specified in Table II. The thicknesses were specified so that a detailed measurement of several plutonium and gallium neutron resonances could be made. The plutonium alloy samples were sealed in double stainless steel containers which could be attached with good thermal conductivity to the cold finger of a temperature controlled closed-cycle He refrigerator.

TABLE I. Isotopic analysis of plutonium.

Isotope	Atomic percentage
^{238}Pu	0.0110
^{239}Pu	93.9273
^{240}Pu	5.8847
^{241}Pu	0.1384
^{242}Pu	0.0388
^{244}Pu	0.0000

We made transmission measurements on these plutonium samples at several temperatures from 15 to 303 K and over a neutron energy range from below 1 to well above 100 eV. Two sets of measurements were made, one set with the 8192 timing channels set at 100 ns, the other at 1000 ns. The low-energy part of the range (below about 25 eV) was covered only by the measurements with 1000 ns timing channels. Above 25 eV only the data with 100 ns timing channels were analyzed. In order to provide information about background and neutron source and detector characteristics, low-energy neutron resonances were measured in a number of other materials. These included a 0.63 mm ^{238}U foil, a 0.1 mm Co foil, and Ta foils 1.0 and 2.0 mm in thickness, W foils 1.0 and 2.0 mm in thickness, and a 2.0 mm In foil. All latter measurements were done at room temperature (about 300 K). Total run times of about 1 h at each temperature were adequate to collect good statistical data on the transmission functions with the detector operating in current mode. In discrete event mode, run times as long as 8 h were used.

A major objective of these measurements is to compare the average quantum vibrational energy of the Ga and the Pu in the Pu-Ga alloys. In order to make this comparison we needed to make careful measurements of the two neutron resonances in Ga near 100 eV. Thus, neutron resonance measurements were made at about 300 K in a 0.081 cm pure Ga

TABLE II. Details of Pu-3.6 at. % Ga alloy samples.

Sample No.	Net wt. (g)	Diameter (cm)	Nominal thickness (cm)	n(Pu) (atoms/b)	n(Ga) (atoms/b)
1	0.47	2.543	0.006	2.296×10^{-4}	8.44×10^{-6}
2	2.63	2.565	0.032	1.262×10^{-3}	4.64×10^{-5}
3	12.60	2.553	0.157	6.107×10^{-3}	2.21×10^{-4}
4	24.61	2.550	0.307	1.195×10^{-2}	4.41×10^{-4}

foil and at various temperatures between 300 and 15 K in a 0.021 cm Ga foil. These foils were fabricated from 99.99% pure orthorhombic α-Ga.

IV. EXPERIMENTAL RESULTS

A. The resolution function and background

Our analysis of the data consists essentially of least-squares fitting of the neutron rate measured by the detector to Eq. (9), the variables in the fitting being some or all of the nuclear resonance parameters and the more important phonon moments. The characteristics of the resolution function $Z(E')$ are very important in this fitting process, and must be considered carefully. Basic parameters governing the resolution function are the proton pulse width, the timing channel width, the angle of the flight path, and the neutron moderation characteristics. The first three are all precisely known. More uncertain is the neutron moderation dispersion time due to the stochastic nature of the slowing-down process in the moderator-reflector assembly of the MLNSC target. This has most recently been studied by Funk *et al.*[21] using neutron transmission by the well-known resonances of ^{238}U and a detector operating in the discrete-event mode. They report that for flight path 5 the dispersion in time of a neutron of precise energy E can be represented by the function

$$p(t)=w_1 f_1(t)+(1-w_1)f_2(t) \tag{10}$$

the functions f belonging to the general χ^2 family

$$f_n(t)=[(t-t_n)^{(\nu-2)/2}/\Gamma(\nu_n/2)\tau_n^{\nu/2}]\exp[-(t-t_n)/\tau_n],\quad t\geqslant t_n,$$
$$=0,\quad t<t_n, \tag{11}$$

and w_1 denotes a weighting factor. The parameter values are

$$\nu_1=6.0, \tag{12a}$$

$$\tau_1(\text{in } \mu\text{s})=0.74/E^{1/2}\text{ eV}, \tag{12b}$$

$$t_1(\text{in } \mu\text{s})=0.49/E^{1/2}\text{ eV}, \tag{12c}$$

$$w_1=0.65, \tag{12d}$$

$$\nu_2=4.3, \tag{12e}$$

$$\tau_2=5.1/E^{1/2}\ \mu\text{s}, \tag{12f}$$

$$t_2=2.2/E^{1/2}\ \mu\text{s}. \tag{12g}$$

We have used this functional form and these parameters without change in our analysis.

The remaining major factor in the resolution function when operating the detector in the current mode is the phosphorescent decay of the scintillator after excitation. Background and long-life decay of these optical modes are intimately connected. They are therefore analyzed together in studying the resonances of thick samples placed in the neutron beam.

The best resonances for this purpose are, in general, those in the cross section of ^{238}U, because their resonance parameters are very well known following decades of study by many groups of workers.[22] The 132 eV resonance of cobalt is also extremely useful because it is very broad and well measured. To obtain background information at energies below the lowest resonance of ^{238}U (6.67 eV), tantalum, tungsten, and indium were used. Finally, plutonium itself provided important self-background data.

From these data, we deduced that the phosphor decay would be described adequately by three exponential decays with the following weights (w) and attenuation periods (τ):

$$w_1=0.095\pm0.006,\quad \tau_1=1.74\pm0.3\ \mu\text{s},$$

$$w_2=0.25\pm0.02,\quad \tau_2=14.1\pm0.4\ \mu\text{s},$$

$$w_3=0.109\pm0.001,\quad \tau_3=233\pm10\ \mu\text{s}.$$

The remainder of the signal is in short decay modes commensurate with or less than the proton pulse width. At short flight times, resonance transmission dips are no more than a few μs wide, and the long τ_3 mode can be incorporated into the background with good approximation. In this case, background fractions vary from 0.36 at 300 μs to 0.19 at 700 μs. At 4000 μs with the long decay modes treated explicitly, the background fraction is 0.048.

B. Gallium resonance parameters and mean phonon energy of gallium metal

We use the resonances of gallium at 96 eV in the cross section of ^{71}Ga and at 111 eV in ^{69}Ga. According to Ref. 22 their widths are known only to between 12 and 25 % accuracy. In order to elucidate the energy of phonons residing on gallium atoms in the Pu-Ga alloy they need to be known with much greater accuracy.

Therefore we made measurements of the gallium resonances at various temperatures between 15 and 300 K on a 0.021 cm thick foil. From analysis of the 96 eV resonance in the data at 294.8 K we obtain a radiation width $\Gamma_\gamma=215\pm6$ meV and a neutron width $\Gamma_n=86.6\pm0.4$ meV. From an analysis that includes the data at 15, 120, and 200 K we obtain a most consistent solution with $\Gamma_\gamma=209\pm4$ meV and $\langle h\nu\rangle=17.4\pm0.4$ meV for the phonon energy.

Analysis of the 15 K data alone gives $\Gamma_\gamma=205\pm6$ meV, $\Gamma_n=84.8\pm0.5$ meV, and $\langle h\nu\rangle=17.9\pm0.7$ meV. With these values, we obtain $\langle(h\nu)^2\rangle=3.6(\pm0.4)\times10^{-4}$ eV^2 and $\langle(h\nu)^2\rangle=3.9(\pm0.8)\times10^{-4}$ eV^2 from the data at 120 and 200 K, respectively.

A similar analysis for the 111 eV resonance gives $\Gamma_\gamma=310\pm5$ meV, $\Gamma_n=53.2\pm0.5$ meV, $\langle h\nu\rangle=17.0$

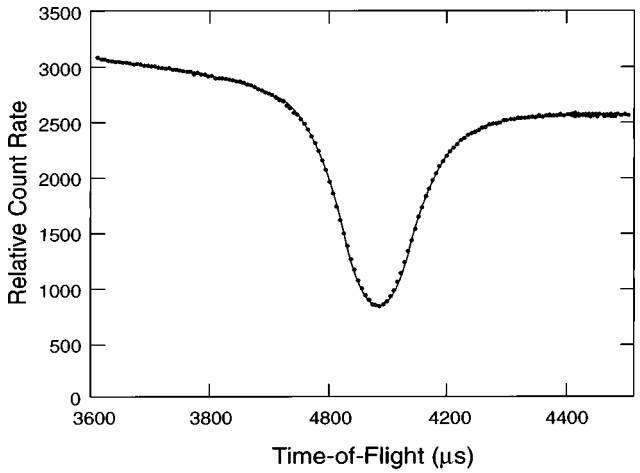

FIG. 1. Fit over ^{240}Pu resonance at 1.056 eV at 303 K, including long decay mode ($Y_1 = 233\ \mu$s). Only one data point in five is shown.

± 0.5 meV. The strong observed isotope effect on the radiation widths for the ^{69}Ga and ^{71}Ga was not apparent in earlier data.

C. Plutonium phonon moments in the Pu-3.6 at. % Ga alloy

The resonances with smallest natural width occur in the cross-sections of the even isotopes of Pu. The prime candidates are the extremely strong 1.056 eV resonance of ^{240}Pu ($\approx 10^5$ b) and the 2.676 eV resonance of ^{242}Pu. The resonance parameters of the former have been measured with great accuracy and found to be $\Gamma_\gamma = 30.27 \pm 0.06$ meV and $\Gamma_n = 2.449 \pm 0.002$ meV.[23] The isotopic abundance of ^{240}Pu in the material used in our experiments is appreciable at 5.885 at. %, and the best information on Doppler broadening will be obtained from the thinnest Pu sample studied (sample No. 1).

Our best fit for the sample No. 1 data at 303 K is shown in Fig. 1. For this fit the moment $\langle h\nu \rangle_T$ was fixed at 53.06 meV. We fit the data at lower temperatures to the moment $\langle h\nu \rangle_T$. The fit for 14.9 K is shown in Fig. 2. The resulting moments are tabulated in Table III and shown graphically in Fig. 3. The curve fitted to these results is a calculation for a

TABLE III. Values of $\langle h\nu \rangle_T$ from the analysis of the 1.05 eV resonance of ^{240}Pu.

Temperature (K)	$\langle h\nu \rangle_T$ (meV)
15	8.3 ± 0.12
60	12.6 ± 0.13
98	18.6 ± 0.16
100	18.4 ± 0.15
200	35.2 ± 0.19

Debye model of the phonon spectrum with a Debye temperature of $\Theta_D = 127.2$ K. The mean phonon energy is $\langle h\nu \rangle = 8.22 \pm 0.12$ meV. The second moment calculated from the 60, 100, and 200 K data is $\langle (h\nu)^2 \rangle = (7.2 \pm 0.3) \times 10^{-5}$ eV^2, which is perfectly consistent with a Debye model of the spectrum.

The isotopic abundance of ^{242}Pu in our samples is reported as only 0.039 at. %. Even though the 2.67 eV resonance is also very strong, the large isotopic dilution results in only a minor dip even in the spectrum of the thickest sample (No. 4). Therefore, for ^{242}Pu we analyzed only the data from this sample. The resonance parameters are not known to be better than 4–7 %. Young and Reeder[24] give $\Gamma_n = 1.99 \pm 0.08$ meV, $\Gamma_\gamma = 25 \pm 1.5$ meV. We have therefore carried out an analysis similar to that used for the gallium resonances, determining the radiation width simultaneously with the phonon moment. Using the neutron width of Ref. 24, we determine from the size of the transmission dip that the actual isotopic abundance is closer to 0.05 at. %. The value adopted for the abundance has some effect on the values of radiation width and phonon moment deduced. Using $f_{242} = 0.0005$ we find a radiation width value $\Gamma_\gamma = 19 \pm 1$ meV and a mean phonon energy $\langle h\nu \rangle = 8.5 \pm 0.5$ meV. Thus the value of the radiation width is considerably smaller than that given by Young and Reeder,[24] and this resonance appears to be the narrowest known amongst all nuclides so far measured. The mean phonon energy derived from the ^{242}Pu resonance is consistent with the more precise value determined from the ^{240}Pu resonance.

D. Ga phonon energy in the Pu-3.6 at. % Ga alloy

The gallium resonances at 95.73 and 111.0 eV are very suitable for measurements of the vibrational energy of gal-

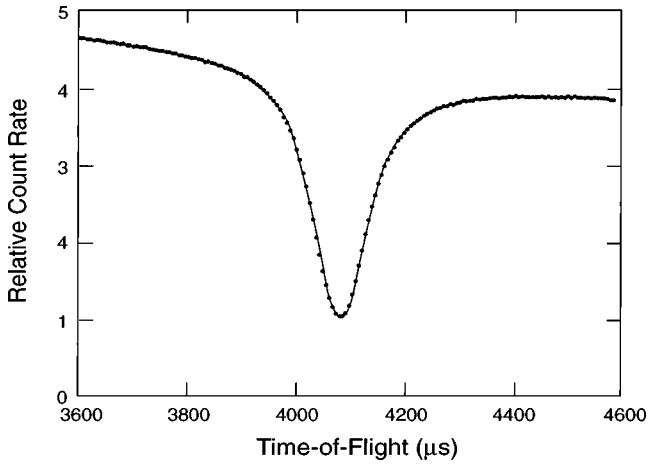

FIG. 2. Fit over ^{240}Pu resonance at 1.056 eV and 15 K; $\langle h\nu \rangle_T = 8.3$ meV.

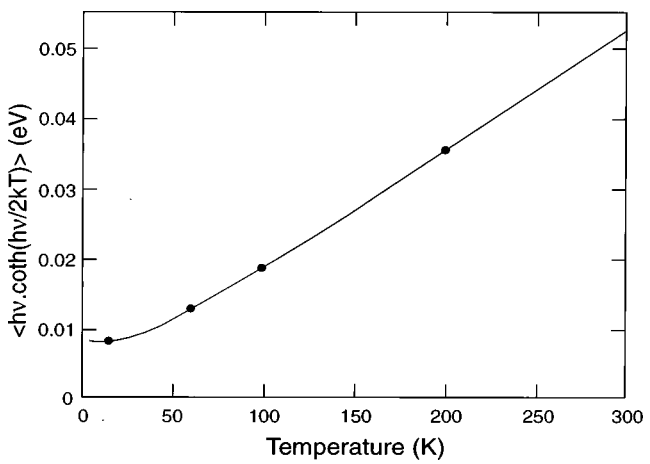

FIG. 3. Plutonium phonon moments $\langle h\nu \rangle_T$ as a function of sample temperature.

lium atoms. In our Pu-Ga alloy (which is largely ^{239}Pu), the analysis of the transmission data is complicated in each case by the presence of a neighboring ^{239}Pu resonance, at 95.51 and 110.55 eV, respectively.[25] Fortunately, the latter resonance is very weak, and if the resonance region cross-sections are weighted by the relative atomic abundances, it is of similar magnitude to the 111 eV gallium resonance. Comparison of the positions of prominent resonances in the 95 to 115 eV region in the gallium and plutonium data sets obtained with identical flight-path indicate that the actual energy separation of the 111 eV Ga resonance and its close ^{239}Pu neighbor is about 0.45 eV, or only about eight 100 ns channels.

Our procedure for obtaining the gallium phonon energy was to calculate the effective cross section, and hence the transmission, over the plutonium resonance and fit the remaining cross section to the gallium resonance using the parameters established in Sec. IV B, the fitted variables being the separation of the gallium and plutonium resonances and the gallium phonon moment $\langle h\nu\rangle_T$. One of the best studies of the ^{239}Pu resonance parameters is due to Derrien and de Saussure,[25] and we have used the parameters determined in that work. ^{239}Pu is a fissile nuclide, and the reaction widths of its resonances contain large fission components. Fission behaves almost as a single channel in the nuclear reaction process and causes the cross sections to deviate considerably from the single-level form of Eq. (2). In calculating the plutonium cross section we have therefore included the many-level interference effects of the six resonances below and above the 110.55 eV resonance. The Doppler broadening of this resonance was calculated using the phonon moments of plutonium determined in Sec. IV C.

In the first stage of fitting the data measured at 303 K with sample No. 4 the gallium parameters were held fixed at the values determined in Sec. IV B, while the energy of the plutonium resonance was varied about its estimated position below the gallium resonance until an optimal fit was achieved. With this energy and all other parameters held fixed the data from sample No. 4 at 20 K were fitted by varying the phonon moment $\langle h\nu\rangle_T$. In a fit to all the data across the transmission dip the resulting value is $\langle h\nu\rangle_T = 17.3 \pm 2.0$ meV (Fig. 4). This value may be distorted by deficiencies in the representation of the plutonium cross-section (in Ref. 25 no uncertainties are quoted on the partial widths). Hence we did a second analysis using only the data across the high-energy wing of the combined transmission dip. This yielded the value $\langle h\nu\rangle_T = 17.8 \pm 2.0$ meV.

This procedure was repeated for the data taken at 61.2, 100, and 200 K. Results for $\langle h\nu\rangle_T$ were 20 ± 3, 26 ± 2.5, and 45 ± 3 meV, respectively. A fit of these values of $\langle h\nu\rangle_T$ to a Debye model gives $\langle h\nu\rangle_T = 19.4 \pm 1.7$ meV. The 20 K datum alone gives 17.8 ± 2 meV. This has only a small model-dependent correction. The higher temperature data then indicate a much higher second moment of the phonon spectrum than implied by a Debye model, but the error on this quantity is large.

Although it is apparent to the eye that two resonances contribute to the transmission dip, at least at the lower temperatures, the maximum possible resolution is obviously desirable. We therefore analyzed carefully the data from the runs with the detector operated in counting mode. The data

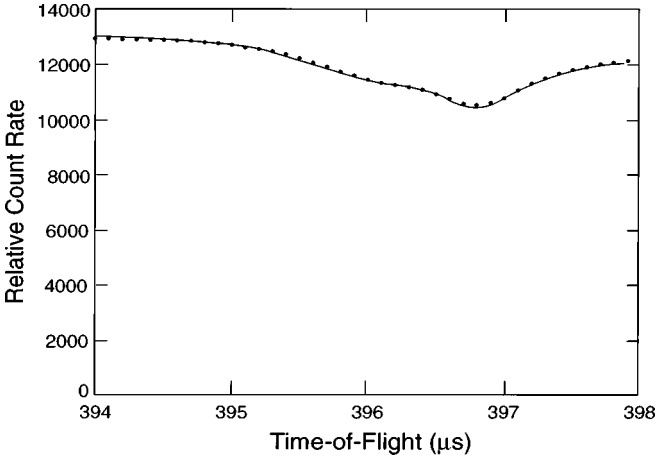

FIG. 4. Gallium and plutonium resonances near 111 eV at 20 K (current mode data).

taken at 304 K indicate a resonance separation of 0.48 ± 0.01 eV. The variables used in the lower temperature runs included both the resonance separation ΔE and the gallium phonon moment. Values found were $\Delta E = 0.45$, 0.45, and 0.46 eV, $\langle h\nu\rangle_T = 15 \pm 2$, 19 ± 2, and 33 ± 3 meV for sample temperatures 15, 100, and 200 K, respectively. The data and fit for 15 K are shown in Fig. 5. These values clearly imply a lower mean value of the phonons on the gallium atoms. A fit of these values of $\langle h\nu\rangle_T$ to a Debye model gives 13.8 ± 1.7 meV. The 15 K datum alone gives $\langle h\nu\rangle = 15 \pm 2$ meV, and the higher-temperature data a low second moment. There are clearly significant differences between the higher-temperature data taken with the detector operating in current and discrete-event modes, and it is not immediately obvious which are the more reliable. A fit to all the data from both detector operation modes gives $\langle h\nu\rangle = 16.3 \pm 1.4$ meV and $\langle (h\nu)^2\rangle = (3 \pm 1) \times 10^{-4}$ eV^2.

V. DISCUSSION

In this work we have used the neutron resonance Doppler broadening to establish the average phonon energies of the plutonium and gallium atoms separately in the δ phase of a Pu-3.6 at. % Ga alloy. This is an application of the neutron

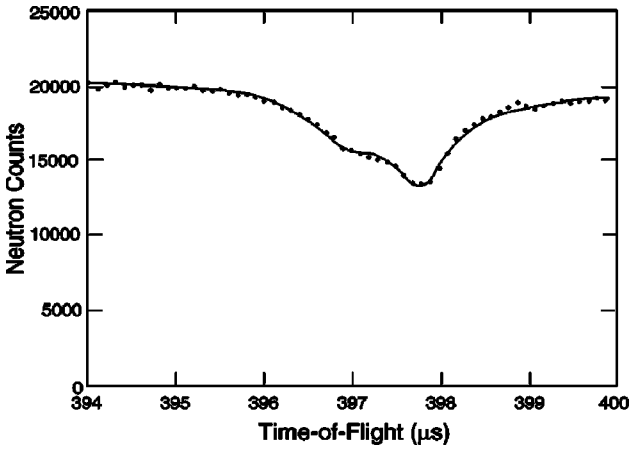

FIG. 5. Gallium and plutonium resonances near 111 eV at 15 K (discrete event data).

Doppler broadening technique to investigate the phonon characteristics of different atomic species in an alloy. We have also measured the phonon energy of α gallium in an effort to improve greatly the accuracy of the resonance parameters of gallium.

The low-temperature mean phonon energy for Ga in α-Ga is measured to be 17.4 ± 0.4 meV from the 96 eV resonance and 17.0 ± 0.5 meV from the 111 eV resonance. The second moment of the phonon spectrum for Ga in α-Ga is $\langle(h\nu)^2\rangle = 3.7\pm0.4\times10^{-4}$ eV^2 based on an average of the higher temperature data from 120 and 200 K. The low-temperature mean phonon energies from the 96 and 111 eV resonances correspond to Debye temperatures of 270 ± 6 and 264 ± 11 K, respectively, with the former value preferred. The second moment is in agreement with this Debye model picture of the spectrum. Specific heat measurements give a value of the effective Debye temperature of 325 K at low temperatures (0.02–4.2 K).[26] As is well known, this value is only valid below about $\Theta_D/50$. Inadequacies in the Debye model in treating the lattice vibrations leads to a sharp drop in the effective Θ_D as the temperature increases, followed by an increase (as in NaCl) or no increase at all (as in the case of Al) as the temperature rises past $\Theta_D/2$.[27] At a temperature corresponding to $\Theta_D/2$, the value of Θ_D is 240 K.[27] We do not know the value of Θ_D at 15 K, but our value of 264–270 K appears reasonable.

The measured first and second moments of the phonon spectrum for Pu in the δ phase of Pu-3.6 at. % Ga alloy [$\langle h\nu\rangle = 8.23\pm0.12$ meV and $\langle(h\nu)^2\rangle = 7.3\pm0.4\times10^{-5}$ eV^2] are consistent with a Debye model with $\Theta_D = 127$ K. This is consistent with the values of the Debye temperatures (127 K for Pu-3.3 at. % Ga and 133 K for Pu-5.9 at. % Ga) obtained by extrapolating elastic constants measured over the 20–300 K temperature range to 0 K.[27] It is also consistent with the value of the Debye-Waller temperature ($\Theta_{DW}=132$ K and generally found to be approximately equivalent to Θ_D) obtained from neutron powder diffraction studies of the temperature dependence of the Debye-Waller factor.[2] The diffraction experiment is equivalent to a determination of the (-1)st moment of the phonon spectrum. Thus the Pu behaves as a Debye solid below room temperature, at least as far as the (-1)st, first and second moments are concerned.

Both of the gallium resonances are uncomfortably close to resonances of ^{239}Pu, thus degrading the accuracy with which we could determine the gallium phonon energy in the Pu-3.6 at. % Ga. In this situation resolution is all important. Therefore we analyzed carefully the data taken with the detector operating in counting mode, even though their statistical quality are much poorer than those taken with the detector in current mode. At 15 K the former data yield a mean phonon energy of 15 ± 2 meV, and at 20 K the current mode data give 17.8 ± 2 meV. The two results are consistent within experimental error, giving us confidence that the interference from the Pu resonance is being correctly simulated. On the basis of the measured Debye temperature for Pu in Pu-3.6 at. % Ga, we would expect, on the basis of weighting by the square roots of the atomic masses, a Debye temperature of 236 ± 3 K for the Ga in the alloy. Instead, we measure a slightly higher value of 255 ± 22 K. Given the large error bounds, it is not clear if this difference is real. Unfortunately, the accuracy that we are able to achieve on $\langle h\nu\rangle_T$ (approximately ±2–3 meV) is quite insufficient to give us very meaningful values for the second moment of the phonon spectrum from the data at intermediate temperatures (60–200 K). Thus we are unable to determine from the present measurements if the gallium atoms are subject to Debye behavior or are in fact vibrating in a simple local mode. This problem will be addressed in future experiments in which the plutonium is comprised largely of the ^{242}Pu isotope, thus greatly ameliorating the interference of the ^{239}Pu resonances.

VI. CONCLUSIONS

We have established a reliable method for measuring certain simple moments of the phonon spectrum with selectivity for atomic species in multielement materials. Background calibrations and detector phosphorescent decay modes were established with the use of ^{238}U, In, Ta, and W foils that were thick enough to black out the transmission of neutrons at several resonances in the cross sections of these materials. In addition, the 1.056 eV resonance of ^{240}Pu revealed the existence of a 233 μs decay mode that was crucial in interpreting the data for this resonance to give the Pu phonon moments. In the course of this work, we also have had to determine more accurate values of the resonance parameters for Ga and ^{242}Pu. For ^{69}Ga and ^{71}Ga, the measured radiation widths show a strong isotope effect that was not apparent in earlier data. For ^{242}Pu, the measured radiation width of the 2.67 eV resonance is considerably smaller than earlier reported, making it to be the narrowest resonance known amongst all nuclides so far measured.

Two major conclusions about the vibrational properties of Pu and Ga in the Pu-Ga alloy can be drawn from this work. (1) The measured first and second moments of the phonon spectrum for Pu in the δ phase of Pu-3.6 at. % Ga alloy are consistent with a Debye model with $\Theta_D = 127\pm2$ K. Thus the Pu behaves as a Debye solid over the temperature range 20–300 K, at least as far as the first few moments are concerned. (2) The effective Debye temperature for Ga in the alloy lies between the expected value based on the Pu Debye temperature and the value of 270 ± 6 K that we measured for pure α-Ga. Given the large error bounds, it is not clear if this means that the Ga in the alloy actually has a higher Debye temperature and therefore is experiencing a stiffer force field than the Pu it replaces. We were unable to measure the second moment of the phonon spectrum of the Ga in the alloy with sufficient accuracy to determine if the Debye form is realistic or if a local Einstein mode exists.

Clearly, much better values of the moments for Ga can be obtained by using a Pu-Ga alloy with less of the interfering ^{239}Pu present. For example, with a sample enriched to 95% in ^{242}Pu, the amount of ^{239}Pu present is only about 2%. This would then reduce the size of the interfering ^{239}Pu resonances by a factor of ≈50 and would allow a clean measurement of both Ga resonances. Given the fact that pure α-Ga has a measured Debye temperature that is only slightly different from what is expected from the Pu Debye temperature, it would be interesting to see how the Debye temperature of In, which is also a δ-phase stabilizer and which has an extremely low Debye temperature of its own ($\Theta_D = 108$ K),[28]

is affected by alloying with Pu (where the Debye temperature for Pu would suggest a Debye temperature for In of 184 K). Both of these experiments are planned for the future.

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