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Atomic thermal vibrations of the light actinide elements

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Abstract

We have been using time-of-flight neutron powder diffraction to determine the Debye–Waller factors of the light actinide elements. The Debye–Waller factor is a measure of the mean-square atomic displacement that arises from the thermal motion of the atoms in any solid. Its temperature dependence determines a Debye–Waller temperature Θ_{DW} that is characteristic of the elastic properties of the solid. The data are obtained by Rietveld analysis of neutron diffraction powder patterns obtained at several temperatures. We have analyzed the results for α-U, α-Np, α-Pu and δ-$Pu_{0.95}Al_{0.05}$. The measured temperature dependence of the Θ_{DW} can be interpreted with an "effective" Grüneisen constant, whose numerical values are much too high to be explained with harmonic forces.

1. Introduction

The primary data in a Debye–Waller experiment are neutron diffraction data that have been fitted with the Rietveld refinement technique [1, 2]. The effect of thermal vibrations on the diffraction pattern is quite strong, with a d spacing dependence that is given by

$$I \alpha \exp\left(-\frac{8\pi^2\langle u^2\rangle}{d^2}\right) \tag{1}$$

so that $\langle u^2\rangle$, the mean-square thermal displacement, is easily determined by Rietveld refinement. $\langle u^2\rangle$ is related to a characteristic parameter of the solid, the Debye–Waller temperature Θ_{DW}, by

$$\langle u^2\rangle_{ideal} = \frac{3\hbar^2 T}{m k_B \Theta_{DW}^2} \times\left(\frac{\Theta_{DW}}{4T} + \frac{T}{\Theta_{DW}}\int_0^{\Theta_{DW}/T}\frac{u\,du}{e^u-1}\right) + \langle u^2\rangle_{offset} \tag{2}$$

where k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and T is the absolute temperature. This is the standard equation for the thermal vibrations of a monoatomic cubic solid [3, 4]; it has been modified by the addition of an extra zero-point motion $\langle u^2\rangle_{offset}$ that is required to fit the data. We believe that the offset is an artifact caused by difficulties in fitting the background neutron scattering in the diffraction patterns. More than one offset is required if data are taken under differing experimental conditions, *e.g.* if both a furnace and a cryostat are used. The offset drops out of the analysis when the temperature dependence of $\langle u^2\rangle$ is considered. Equation (2) is too simple to be correct in principle for a real actinide structure. However, it seems to give useful results in practice.

We have found that it is necessary to allow Θ_{DW} to be slightly temperature dependent. This is necessary in principle to allow for the changes in the elastic constants that are induced by the volume changes that accompany ordinary thermal expansion, an effect described by the Grüneisen constant in the quasi-harmonic approximation of lattice dynamics. We have made the empirical assumption that

$$\Theta_{DW} = \Theta_{DW,0} + cT \tag{3}$$

Our results for α-U, α-Np, α-Pu and δ-$Pu_{0.95}Al_{0.05}$ are shown in Fig. 1. The lines through the data are fits to eqns. (2) and (3), and the fitted offsets have been suppressed. The fitted values are shown in Table 1. Data involving the temperature dependence of Θ_{DW} can be analyzed in terms of the Grüneisen constant γ_G. In terms of the phonon frequencies, the Grüneisen constant is given by

$$\frac{\Delta\omega}{\omega} = \gamma_G\frac{\Delta v}{v} = -\gamma_G\chi T \approx \frac{\Delta\Theta_{DW}}{\Theta_{DW}} \tag{4}$$

where $\Delta\omega/\omega$ is the relative change in phonon frequencies, and $\Delta v/v$ is the relative volume change. Numerical values of the Grüneisen constant are usually in the range 1–2, so there is always some temperature dependence to be expected in Θ_{DW}. An additional tem-

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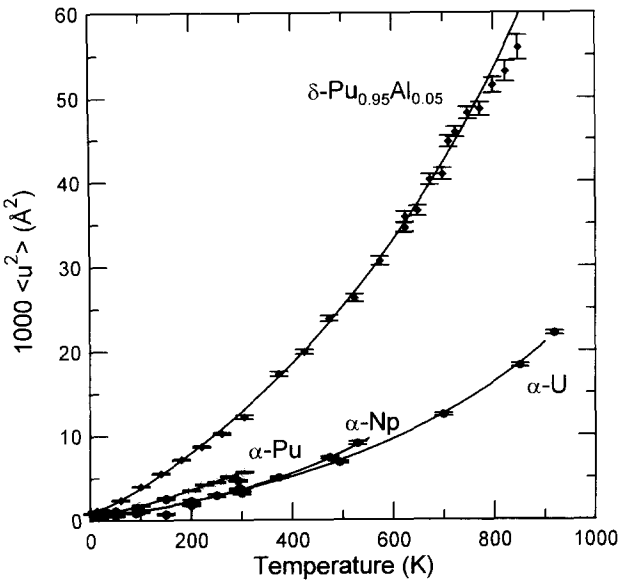

Fig. 1. Mean-square thermal vibrations *vs.* temperature of the light actinide elements. The fit through the points is described in the text.

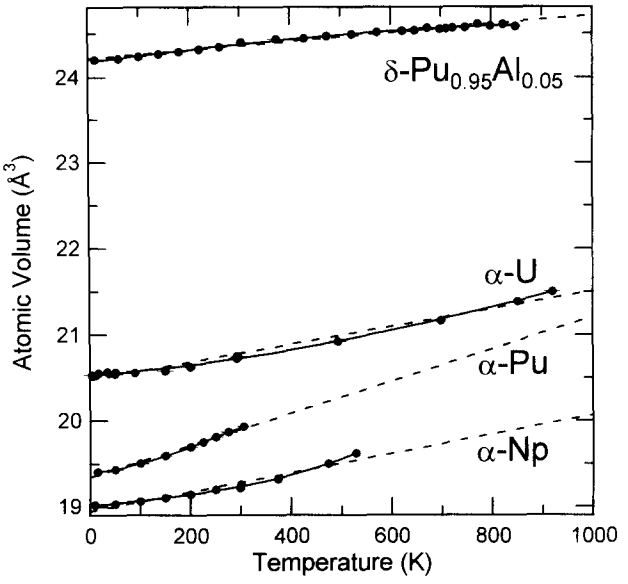

Fig. 2. Atomic volumes *vs.* temperature of the light actinide elements. – – –, linear approximations to the thermal expansion.

TABLE 1. Debye–Waller parameters and effective Grüneisen constants of the light actinide elements

	References	$\Theta_{DW,0}$ (K)	c	χ ($\times 10^{-6}$ K^{-1})	γ_{eff}
α-U	5, 6	260(4)	−0.109(4)	50.2	8.3
α-Np	7, 8	269(10)	−0.15(2)	59.3	9.4
α-Pu	9	201(5)	−0.08(2)	96.4	4.1
δ-Pu	10	132(1)	−0.047(1)	20.3	17.5

perature dependence in Θ_{DW} can result from the anharmonicity arising from a quadratic term in the interatomic potential; the functional temperature dependence of Θ_{DW} is in this case the same as in the quasi-harmonic theory, so that the two are not distinguishable experimentally by our technique. We can, however, define an "effective" Grüneisen constant γ_{eff} from experimentally determined values:

$$\gamma_{eff} = -\frac{c}{\chi \Theta_{DW}} \quad (5)$$

Values of χ and γ_{eff} are given in Table 1. The experimental values of χ are determined by linear approximation to the atomic volumes derived from our diffraction data, shown in Fig. 2.

The main point of Table 1 is that all the values of γ_{eff} are much larger than can be expected from the quasi-harmonic effect. We conclude from this that true anharmonic effects may be important in explaining the unusual lattice behavior, both in Θ_{DW} and in χ, of the light actinide metals.

Acknowledgments

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