

Neutron Diffraction Study of Thermal Parameters in UX_3 Compounds

BY J. FABER JR AND G. H. LANDER

Argonne National Laboratory, Argonne, IL 60439, USA*

P. J. BROWN

Institut Laue–Langevin, 156X, 38042 Grenoble, France

AND A. DELAPALME

Laboratoire Leon Brillouin, Orme des Merisiers, 91190 Gif-sur-Yvette, France

(Received 17 July 1980; accepted 27 January 1981)

Abstract

The intensities of the weak superlattice reflections in the UX_3 compounds, where $X = Ru, Rh, Ge,$ and Sn , have been measured by neutron diffraction. These compounds have the ordered $AuCu_3$ structure. Excellent fits to the observed intensities are obtained by introducing anisotropic second-order and fourth-order (anharmonic) terms to describe the probability distribution function at the X atom site. The ratio of the magnitude of the mean-square thermal vibration parallel to and perpendicular to the unique tetragonal axis of the X atom appears to depend on whether p bonding (UGe_3, USn_3) or d bonding (URu_3, URh_3) occurs with the U electrons. In UGe_3 data out to $Q = 13 \text{ \AA}^{-1}$ show the need to include a fourth-order anharmonic term. The form of this anharmonicity suggests an attractive potential between the nearest-neighbor U– X atoms.

I. Introduction

Neutron diffraction is particularly well suited to the determination of accurate thermal parameters because the neutron–nuclear interaction exists over a very short range. This means that nuclear scattering extends to high $|Q|$, the momentum transfer, where the effects of thermal motion are readily apparent. One hopes, therefore, to extract reliable thermal parameters from neutron measurements without the need for corrections for the form factor, anomalous dispersion, and absorption, which complicates X-ray studies. Atomic thermal parameters are invariably considered within the harmonic approximation, although the observation that solids expand contradicts this assumption. However, higher-order corrections to the harmonic approxi-

mation, which give information about the restoring potentials in the solid, are usually small and difficult to establish from elastic scattering experiments. To perform such analyses, diffraction data of high precision are required out to large values of $|Q| = 4\pi \sin \theta / \lambda$, where θ is the Bragg angle and λ the radiation wavelength. An excellent survey of such measurements is given by Willis (1969).

In this paper we report on neutron diffraction studies of $URu_3, URh_3, UGe_3,$ and USn_3 at room temperature (and below for UGe_3). Our original motivation for studying UGe_3 was to determine the scattering amplitudes and thermal parameters to use in processing the results of a companion polarized-neutron study (Lander, Reddy, Delapalme & Brown, 1980). The study with unpolarized neutrons demonstrated strikingly the importance of an anisotropic second-order term in the Debye–Waller factor of the Ge atom. To our knowledge such an effect has not been previously reported in this common structure. We then studied the other materials and undertook a search for higher-order anharmonic effects.

II. Experimental details

All experiments discussed here have used conventional four-circle neutron diffractometers. At Argonne National Laboratory we used a Be (11.0) reflection with $2\theta_M = 55^\circ$ to give a wavelength of 1.05 \AA . Neutron experiments at the Institut Laue–Langevin used the D9 diffractometer on the hot source. A Cu monochromator reflecting from the (200) planes was used to give a wavelength of 0.84 \AA .

Single crystals in the shape of cylinders (about 2–3 mm in diameter and about 10 mm long) were examined. To minimize the variation of the neutron path length through the crystal, data were collected in such a way as to keep the scattering vector more than

* Work supported by the US Department of Energy.

60° from the long axis of the cylinder. Usually up to 50% of the total equivalent set of reflections could be measured; these were then averaged, corrected for absorption (appreciable for URh₃ only), and geometric effects. The agreement within equivalent sets was always good and the error bars in the figures correspond to standard deviations.

The most significant experimental difficulty is connected with second-order ($\lambda/2$) contamination. In the AuCu₃ structure there are two types of structure factors, the fundamental set corresponding to face-centered lines (*i.e.* h,k,l all even or all odd) or the so-called superlattice lines with h,k,l mixed indices. For the generic formula UX₃ the fundamental structure factor is $b_U + 3b_X$, neglecting thermal parameters, whereas the superlattice structure factor is $b_U - b_X$. As we shall see, the fundamental intensities are between 10² and 10⁴ stronger than the superlattice ones. At every superlattice position the $\lambda/2$ contribution from a fundamental reflection contributes, and therefore must be reduced or eliminated. At ANL we used a ²³⁹Pu filter and measured $I_0(\lambda/2)/I_0(\lambda) = 4 \times 10^{-4}$, where I_0 refers to an incident intensity. This value resulted in corrections of ~20% for the low-angle reflections in UGe₃, but rapidly decreased with increasing Q , and negligible corrections for the other compounds. At ILL an Er filter of 1 mm was sufficient to eliminate completely the $\lambda/2$ component.

III. Analytical expressions

The atomic structure of these compounds is the AuCu₃ ($L1_2$) type (Fig. 1), space group $Pm3m$ (No. 221) with the atoms in positions

| | | | | |
|---|---|-----|---------|--------------------------------------------------------------------|
| U | 1 | (a) | $m3m$ | 000 |
| X | 3 | (c) | $4/mmm$ | $0\frac{1}{2}, \frac{1}{2}0\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$. |

The treatment of Willis (1969) is confined to point groups having cubic symmetry, in which case the concept of a constant potential at a given radius vector is useful. However, for point groups of lower symmetry

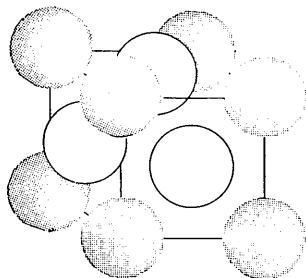


Fig. 1. AuCu₃ structure of all four UX₃ compounds discussed in this paper. The U atoms (shaded circles) are at the cube corners and the X atoms (open circles) are at the face-centered positions.

it is more useful to consider the general form of the probability density function, as given for example by Johnson (1970).

The probability density function may be expanded as

$$\psi(\mathbf{t}; {}^1\kappa, {}^2\kappa, {}^3\kappa, {}^4\kappa, \dots) = \exp\left(i {}^1\kappa^j t_j + \frac{i^2}{2!} {}^2\kappa^{jk} t_j t_k + \frac{i^3}{3!} {}^3\kappa^{jkl} t_j t_k t_l + \dots\right),$$

where ${}^s\kappa$ are cumulant tensors of rank s and \mathbf{t} is the atomic position vector with components t_j, t_k , etc. Symmetry will then immediately allow us to define the number of terms, the harmonic approximation being equivalent to terminating the expansion at the second-order tensor ${}^2\kappa$. From Table 9.1 of Johnson (1970) we then have

| | | ${}^1\kappa$ | ${}^2\kappa$ | ${}^3\kappa$ | ${}^4\kappa$ |
|---|---------|--------------|--------------|--------------|--------------|
| U | $m3m$ | 0 | 1 | 0 | 2 |
| X | $4/mmm$ | 0 | 2 | 0 | 4. |

The absence of odd-order terms simply reflects the fact that both point groups are centrosymmetric.

To determine the exact form of the cumulant tensors it is convenient to use Tables 4a-f in Birss (1964). We are interested in polar tensors so that for the U site ($m3m$) the tensors are \mathbf{T}_2 and \mathbf{T}_4 , and for the X site ($4/mmm$) they are \mathbf{H}_2 and \mathbf{H}_4 . Following Birss (1964), and performing the necessary Fourier transform into reciprocal space (Willis & Pryor, 1975), the relevant second-order thermal parameters are

$$\beta^U(h_1 h_1 + h_2 h_2 + h_3 h_3)$$

and

$$\beta_{11}^X(h_1 h_1 + h_2 h_2) + \beta_{33}^X(h_3 h_3). \quad (2)$$

The scattering vector \mathbf{Q} is expanded into its three components

$$\mathbf{Q} = 2\pi(h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^*),$$

where \mathbf{a}_i^* are the reciprocal-lattice basis vectors. Expression (2) gives the familiar temperature factors in the harmonic approximation. Since the z axis is defined as the unique axis in the tetragonal point group this expression refers explicitly to the atom at $(\frac{1}{2}\frac{1}{2}0)$. The term β^U is related to the isotropic uranium temperature factor B_U so that

$$4a^2 \beta^U = B_U = \frac{8\pi^2}{3} \langle u^2 \rangle_U,$$

where $\langle u^2 \rangle_U$ is the mean-square displacement of the U atom. We see, therefore, that the term β_{11} for the X atom refers to harmonic motion within the plane of the nearest-neighbor fourfold coordination of U atoms, whereas the β_{33} term refers to motion perpendicular to this plane towards the vacant position $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$.

For the fourth-order terms we must consider tensors T_4 and H_4 of Birss (1964). The T_4 tensor gives two parameters δ_1^U and δ_2^U

$$\delta_1(h_1^4 + h_2^4 + h_3^4) + 3\delta_2(h_1^2 h_2^2 + h_2^2 h_3^2 + h_3^2 h_1^2). \quad (3)$$

These parameters δ_1 and δ_2 can be related to the parameters γ and δ of Willis [1969; see equation (4.11)], and will define a potential as shown in Fig. 4 of Willis (1969) with lobes pointing along the $\langle 100 \rangle$ or $\langle 111 \rangle$ directions.

For the X atom, four independent parameters are required to determine the anharmonic potential. According to the tensor H_4 the expression is

$$\delta_1(h_1^4 + h_2^4) + \delta_2 h_3^4 + 3\delta_3 h_1^2 h_2^2 + 3\delta_4 h_3^2(h_1^2 + h_2^2). \quad (4)$$

A simplification occurs if $\delta_2 = \delta_4 = 0$ and $\delta_3 = -\delta_1$ since the fourth-order term then becomes

$$\delta_1(h_1^4 + h_2^4 - 3h_1^2 h_2^2) = \frac{2}{3}\delta_{xy}[h_1^4 + h_2^4 - \frac{2}{3}(h_1^2 + h_2^2)^2] \quad (5)$$

and δ_{xy} is related to the term δ defined by Willis (1969) except that the modulation of the potential is now within the (001) plane.

The atomic positions in the $AuCu_3$ structure are such that the structure factors fall into two groups.

(i) Fundamental reflections with $h_1 (=h)$, $h_2 (=k)$, and $h_3 (=l)$ all even or all odd with the nuclear structure factor

$$F_f = b_U T_U(\mathbf{Q}) + 3b_X T_X(\mathbf{Q}), \quad (6)$$

where b_U and b_X are the nuclear scattering potentials of the U and X atoms, respectively, and $T_U(\mathbf{Q})$ and $T_X(\mathbf{Q})$ are the corresponding thermal parameters. For small $|\mathbf{Q}|$, both T_U and T_X are near unity and with b_U and b_X both positive these reflections are strong and relatively insensitive to the exact form of $T(\mathbf{Q})$.

(ii) The superlattice reflections with mixed indices have a nuclear structure factor

$$F_s = b_U T_U(\mathbf{Q}) - b_X T_X(\mathbf{Q}). \quad (7)$$

If we can arrange $b_U \simeq b_X$ then the reflection intensity will be weak but very sensitive to the exact form of $T(\mathbf{Q})$.

IV. Results and analyses

UGe₃

Since the most extensive measurements have been taken on UGe₃, we shall discuss this first. The refinement results are summarized in Table 1, and the individual fits illustrated in Figs. 2–5. Fig. 2 shows the importance of the cancellation occurring in (7). Notice first that the scale is logarithmic. The intensities of the weak superlattice reflections are $\sim 10^{-4}$ of the strong fundamental reflections. The latter suffer from $\sim 15\%$

Table 1. Results of refinements of superlattice reflections for UGe₃

$a = 4.206 \text{ \AA}$, $b_U = 0.852 + 10^{-14} \text{ m}$, $b_{Ge} = 0.819 \times 10^{-14} \text{ m}$, $B_U = 0.28 \text{ \AA}^2$ at 290 K and 0.15 \AA^2 at 150 K. S is the scale factor depending on instrumental constants, β_{11} and β_{33} are defined for the Ge atom as in (2). δ_{xy} for Ge is defined in (5). χ^2 is defined in the text.

| Data set | S | β_{11} ($\times 10^{-4}$) | β_{33} ($\times 10^{-4}$) | δ_{xy} ($\times 10^{-5}$) | χ^2 |
|-----------|--------------|--------------------------------------|--------------------------------------|---------------------------------------|----------|
| ANL 293 K | 165 ± 12 | 59 ± 3 | 80 ± 4 | 0 | 1.4 |
| ANL 293 K | 171 ± 12 | 55 ± 3 | 78 ± 4 | 3.0 ± 0.8 | 0.8 |
| ILL 293 K | 67 ± 7 | 49 ± 3 | 63 ± 5 | 0 | 2.4 |
| ILL 293 K | 80 ± 7 | 44 ± 2 | 56 ± 2 | 0.94 ± 0.14 | 1.2 |
| ILL 150 K | 57 ± 4 | 26 ± 1 | 37 ± 2 | 0.33 ± 0.09 | 0.9 |

extinction, the corrected intensities falling nearly on a straight line as a function of Q^2 , and are not affected within the present precision by either the second- or fourth-order terms in $T(\mathbf{Q})$. The superlattice reflections increase in intensity with increasing $|\mathbf{Q}|$ because the thermal vibration of the Ge atom is greater than that of

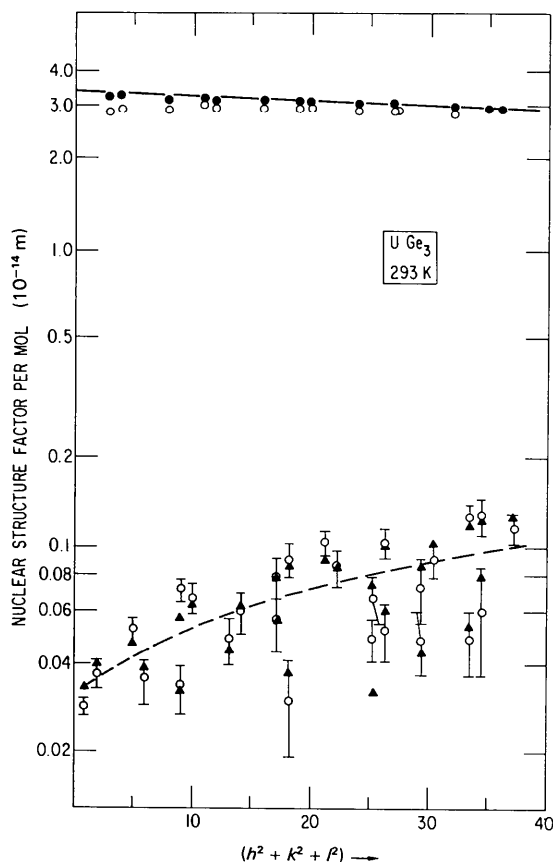


Fig. 2. Observed (open points) structure factors plotted against $h^2 + k^2 + l^2 = a^2 Q^2 (4\pi^2)^{-1}$ for UGe₃ for the ANL data set. The solid circles correspond to the strong fundamental reflections after extinction corrections, the solid line defining their calculated position. The solid triangles are the calculated structure factors for the weak superlattice reflections. The dashed curve corresponds to the values expected if $\beta_{11} = \beta_{33}$ and $\delta_{xy} = 0$.

uranium. However, the anisotropy in the observed structure factors is a direct consequence of $\beta_{11} \neq \beta_{33}$ in (2).

The usual crystallographic least-squares analysis does not include fourth-order terms in the temperature factor so we have written a program explicitly for the AuCu_3 structure incorporating these effects. One immediately obvious fact is that the weak reflections alone are sufficient to define β_{11}/β_{33} and the δ parameters to a high degree of precision. The strong reflections, taken together with the weak, define b_U/b_{Ge} and, to a certain extent, the absolute values of β_{11} and B_U . In our studies of UGe_3 we are unable to reconcile the ratio $(F_f/F_s)_{Q=0}$ with the accepted scattering lengths of 0.843 and 0.819×10^{-14} m for U and Ge, respectively. Assuming the value for Ge is correct, we require $b_U = 0.852 \times 10^{-14}$ m, as opposed to the value of $(0.843 \pm 0.002) \times 10^{-14}$ m given by Cooper, Sakata & Rouse (1979). Fortunately, the present investigations are *not* dependent on accurate scattering lengths since they may be thought of as analyzing the *differences* about the dashed line (as in Fig. 2) as a function of Q .

In Fig. 3 we plot $|F_o| - |F_c|$ versus the same quantity $h^2 + k^2 + l^2$. Fig. 3(a) is a refinement with no fourth-order term. The χ^2 is 1.4 for this refinement, where

$$\chi^2 = (m - n)^{-1} \sum \{(|F_o| - |F_c|)/\Delta F_o\}^2.$$

F_o and F_c are observed and calculated structure factors, respectively, ΔF_o is the standard deviation in F_o , m is

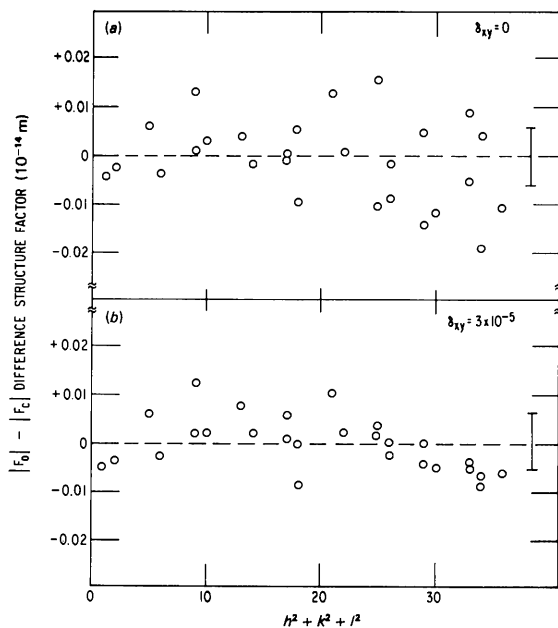


Fig. 3. Difference structure factors for UGe_3 (ANL 293 K) superlattice reflections versus $h^2 + k^2 + l^2$. The fourth-order term is included in (b), $\chi^2 = 0.8$, but not in (a), $\chi^2 = 1.4$.

the number of reflections, and n the number of variables. The least-squares program minimizes χ^2 . The addition of a fourth-order term δ_{xy} (see equation 5) for the Ge atom resulted in a significant reduction in χ^2 . This additional parameter clearly improves the agreement at high Q .

The results for refinements of data taken at the ILL out to high $|Q|$ at 293 and 150 K are shown in Figs. 4 and 5, and the parameters are given in Table 1. Since the ILL data extend to higher Q values than those at ANL, they should be more reliable. In both sets we find $\beta_{33}/\beta_{11} > 1$, the actual value of this ratio at 293 K being 1.42 ± 0.08 from the ANL data and 1.27 ± 0.05 from the ILL data. The fourth-order term δ_{xy} is also positive in both cases and results in a decrease in χ^2 . There is some deviation in the absolute values, possibly as a consequence of systematic errors. We have also performed a number of analyses on the ILL data to

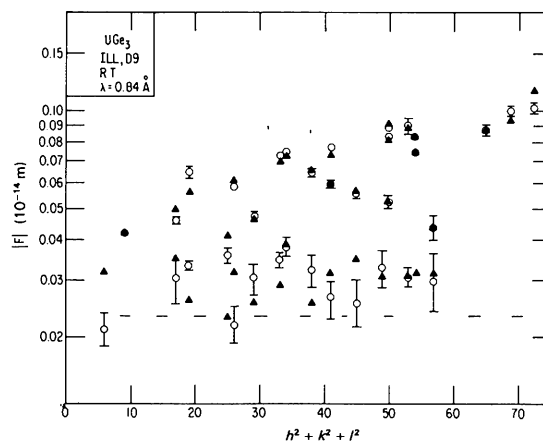


Fig. 4. Structure factors vs $h^2 + k^2 + l^2$ for superlattice reflections for UGe_3 (ILL 293 K). The open points are from experiment, the closed triangles are from the calculation. The horizontal dashed line is the approximate lower level of observation; note logarithmic scale.

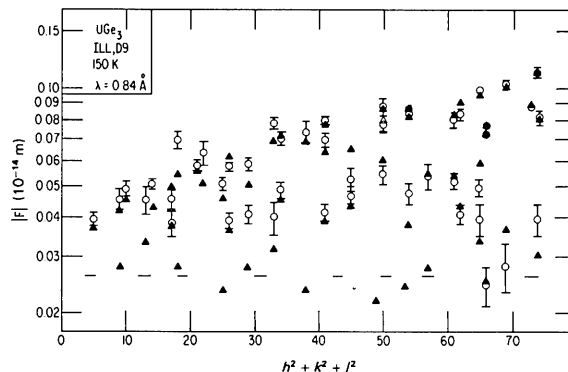


Fig. 5. Same as Fig. 4 but at 150 K. As in Fig. 4 reflections with intensities lower than the dashed horizontal line could not be measured reliably, but their calculated structure factors (solid triangles) are always small.

vary δ_i ($i = 1-4$) in (4). These did not give significant improvements in χ^2 . Allowing all δ_i 's to vary gave significant values for $\delta_1 = (1.2 \pm 0.3) \times 10^{-5}$ and $\delta_3 = (-0.8 \pm 0.2) \times 10^{-5}$ only, and it was on this basis that we set $\delta_3 = -\delta_1 = \delta_{xy}$. Furthermore, no significant fourth-order term was found for the U atom. As a further test of the significance of the δ_{xy} term, we have examined the correlation matrix in the refinement involving S , β_{11} , β_{33} , and δ_{xy} (in Table 1). The correlations between S and the second-order thermal coefficients β_{11} and β_{33} are high (>0.9 ; this correlation may be reduced by also using the strong reflections in the refinement), but none of the parameters are correlated with δ_{xy} more than 0.4.

The absolute values of both the β_{ii} coefficients and δ_{xy} decrease as the temperature is reduced to 150 K. This is as expected; in fact $\beta_{ii} \propto T$ and $\delta_{xy} \propto T^3$ (approximately) from theory, and within the rather poor statistics of the data we do see a faster decrease of δ_{xy} than β_{ii} . Of course, these expectations are strictly valid only at higher temperatures when the zero-point motion is insignificant. An interesting trend is that the ratio β_{33}/β_{11} appears independent of temperature, reflecting presumably this tendency for the zero-point motion as well. In a separate experiment designed to examine selected reflections we verified that this is indeed the case even at 4.2 K, and this information was used in processing the polarized-beam experiments (Lander *et al.*, 1980).

USn₃

The results for USn₃ are shown in Fig. 6. With both strong and weak reflections shown in Fig. 6 we obtain excellent agreement (R factor 1.9%) with complete stoichiometry and $B_U = 0.71 \pm 0.03 \text{ \AA}^2$ for the U temperature factor. The complete parameters are given in Table 2. Within the accuracy of the data $\delta_{xy} = 0$. Since $b_U - b_{Sn}$ is fairly large, the weak reflections appear to behave 'normally' on a logarithmic plot *versus* Q^2 , *i.e.* they decrease. Note, however, the substantial scatter about the dashed line in Fig. 6, which shows directly the presence of anisotropic thermal motion at the Sn site.

URu₃ and URh₃

The results for URu₃ and URh₃ are shown in Figs. 7 and 8, respectively, and are also given in Table 2.

In the cases of URu₃ and URh₃, the method of producing these crystals by electron-beam zone refining leads to highly perfect crystals which exhibit very large extinction effects. We have discussed this point at length in a study of URh₃ with polarized neutrons (Delapalme, Lander & Brown, 1978). In the present work we have not measured the strong fundamental reflections, but, as discussed earlier, this does not affect the parameters of Table 2. The superlattice reflections are too weak to suffer extinction effects.

We note immediately in Table 2 that for both URu₃ and URh₃ the ratio $\beta_{33}/\beta_{11} < 1$, in contrast to the situation for UGe₃ and USn₃. With the data and Q range examined we find no significant fourth-order term in either URu₃ or URh₃.

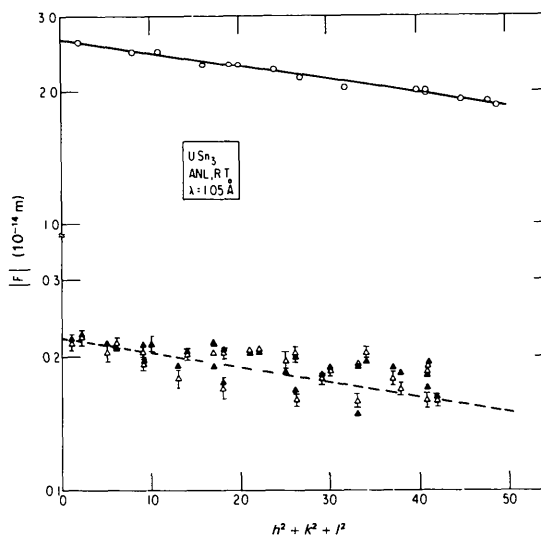


Fig. 6. Observed structure factor (open points) and calculated values (solid line for fundamental and closed triangles for superlattice) for USn₃ as a function of $h^2 + k^2 + l^2$. The dashed line indicates the expected values for the superlattice reflections if the thermal motion of the Sn atom was isotropic.

Table 2. Results of refinements for UX_3 systems

The parameters are as in Table 1, with β_{11} , β_{33} , and δ_{xy} referring to the X atom. To compare B_U with β_{ii} the effective temperature factor is given by $B = 4a^2 \beta_{ii}$.

| | a (\AA) | b_X ($\times 10^{-14}$) | B_U (\AA^2) | β_{11} ($\times 10^{-4}$) | β_{33} ($\times 10^{-4}$) | β_{33}/β_{11} | δ_{xy} ($\times 10^{-5}$) | χ^2 |
|------------------|-------------------------|--------------------------------|-----------------------------|--------------------------------------|--------------------------------------|-------------------------|---------------------------------------|----------|
| URu ₃ | 3.980 | 0.721 | 0.25 | 42 \pm 1 | 40 \pm 1 | 0.95 \pm 0.04 | 0 \pm 0.7 | 0.6 |
| URh ₃ | 3.988 | 0.584 | 0.25 | 51 \pm 1 | 39 \pm 1 | 0.76 \pm 0.04 | -1 \pm 1.0 | 1.2 |
| UGe ₃ | 4.206 | 0.819 | 0.28 | 44 \pm 2 | 56 \pm 2 | 1.27 \pm 0.05 | 0.94 \pm 0.14 | 1.2 |
| USn ₃ | 4.626 | 0.622 | 0.71 | 80 \pm 3 | 100 \pm 3 | 1.25 \pm 0.07 | -1 \pm 3 | 0.8 |

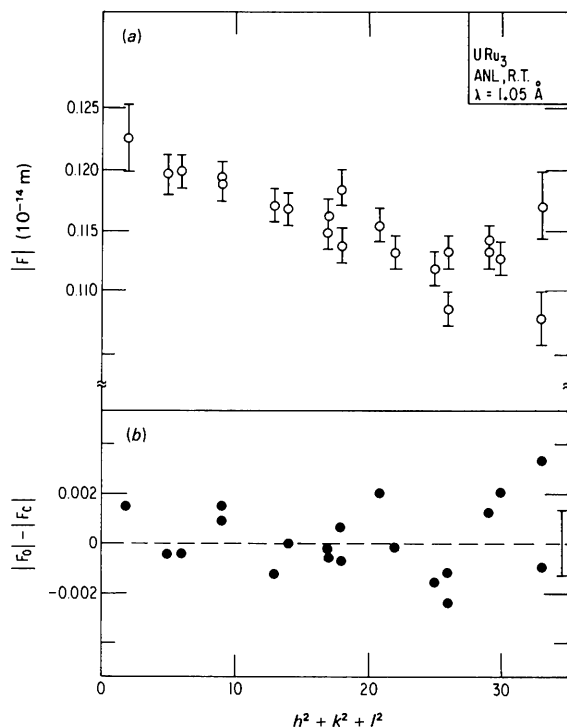


Fig. 7. (a) Observed structure factors for URu_3 as a function of $h^2 + k^2 + l^2$; (b) the difference $|F_0| - |F_c|$; note the different ordinate scales.

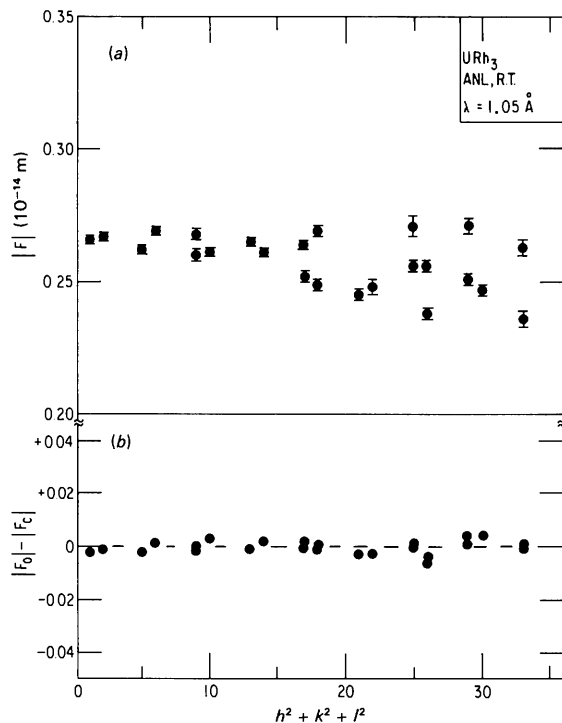


Fig. 8. Observed structure factors as a function of $h^2 + k^2 + l^2$ for URh_3 . (a) and (b) as in Fig. 7.

V. Discussion

In these experiments we have measured the weak superlattice reflections from a number of uranium compounds with the AuCu_3 ordered structure. The results show quite clearly the need to consider anisotropic thermal vibrations at the X atom site in all cases. To our knowledge this simple fact, which is permitted by symmetry, has not been reported heretofore, no doubt partly because of the difficulty of measuring these reflections. The structure factors are in all cases $\leq 0.3 \times 10^{-14}$ m per formula unit and for UGe_3 are much smaller. Accordingly, the intensities are similar to those of acoustic phonons and we require an integrated intensity accurate to $\sim 10\%$. The most serious experimental difficulty is the elimination of second-order contamination. Another potential problem arising from thermal diffuse scattering (TDS) is not serious. The reason for this is that TDS arises principally from one-phonon scattering associated with the acoustic modes of vibration and at the superlattice reciprocal-lattice points the low-energy acoustic modes are *out-of-phase* acoustic phonons. Their structure factor is correspondingly very small. TDS does arise from optic phonons, which will have a large structure factor at the reciprocal-lattice points of interest, but they are at 2–4 THz in energy, and the scattering conditions are such that they will not be sampled in our experiments. Another problem is the possibility of partial lattice disorder in the AuCu_3 structure. We have no evidence from our experiments that these are not ordered stoichiometric compounds. This is further reinforced by the observation of de Haas–van Alphen effects in both URh_3 (Arko *et al.*, 1975) and UGe_3 (Arko & Koelling, 1978) and this effect cannot be observed if disorder is present in the crystals.

We believe the change in magnitude of β_{33}/β_{11} between URu_3 and URh_3 on the one hand, and UGe_3 and USn_3 on the other, shows the importance of bonding effects on the interatomic restoring potentials. The outermost electrons in Ge and Sn are in p states and their interaction with the outermost $5f$ – $5d$ electrons of the U atom will be predominantly *along* the $\langle 110 \rangle$ directions. As a result a strong (001) network is formed (see Fig. 1) between an X atom and its four nearest neighbors, and this qualitatively predicts $\beta_{33}/\beta_{11} > 1$, as observed. On the other hand, the outermost electrons in Ru and Rh are $4d$ states that give rise to potentially strong π -type bonding with the U states, consistent with $\beta_{33}/\beta_{11} \leq 1$. Of course, these arguments are far too simple to have other than qualitative validity in these complex systems, and detailed considerations of the interatomic potentials involving the basis wavefunctions are now in progress at Argonne National Laboratory (Koelling, 1980).

In one material, UGe_3 , we have found evidence for a fourth-order term in the thermal parameter of the Ge

atom. However, from Table 2 we see that the anharmonic parameter in UGe_3 is similar in magnitude to the error bars on δ_{xy} of the other materials. Thus, in UGe_3 it seems probable that the availability of higher- Q data and the almost complete cancellation of b_U and b_{Ge} give greater sensitivity, rather than δ_{xy} being especially significant in UGe_3 .

We now examine the significance of these higher-order terms in the thermal parameters. The latter are, of course, related to the potential acting on a given atom so that higher-order terms signify anharmonicity (*i.e.* the restoring potential can no longer be regarded as proportional to the square of the atomic displacement from the mean position). It should be realized at the outset that the thermal parameters are an ensemble average over the total potential energy of the crystal, considered as a collection of coupled anharmonic oscillators. To draw physical significance from the parameters we must make the assumption that the system can be treated as a collection of independent anharmonic oscillators. Furthermore, the problem of writing down a tractable potential is feasible only if we follow Willis (1969) and adopt the high-temperature (classical) limit. In the case of cubic symmetry Willis (1969) has shown that the potential to fourth order can be written in the form

$$V(u_1, u_2, u_3) = V_0 + \frac{1}{2}ar^2 + \gamma r^4 + \beta u_1 u_2 u_3 + \delta(u_1^4 + u_2^4 + u_3^4 - \frac{3}{5}r^4), \quad (8)$$

where u_1, u_2 , and u_3 are Cartesian coordinates, $r^2 = u_1^2 + u_2^2 + u_3^2$, a is the coefficient of the harmonic potential, and the other terms give the anharmonic contribution. The anisotropic term in δ represents the influence of the local crystalline field in producing an angular dependence of the potential and is written in such a way that the average value over the surface of a sphere is zero. In principle, one could develop an expression similar to (8) for the tetragonal point-group symmetry of interest here, but this is very tedious, and will introduce a number of normalization conditions that make it difficult to identify the isotropic and anisotropic parts of the fourth-order potential.

Since the point-group symmetry is centrosymmetric, $\beta = 0$, but we must introduce two parameters α_{\parallel} and α_{\perp} which refer to the harmonic (second-order) potential parallel and perpendicular to the local tetragonal axis, respectively. Similarly for the fourth-order terms new terms in γ should be introduced, but the experimental evidence is for a modulation of the potential in the (001) plane, and thus we equate all γ 's to zero. The anisotropic term in δ must then average to zero over the circumference of a circle and can readily be shown to be of the form $\delta(u_1^4 + u_2^4 - 6u_1^2 u_2^2)$. The full potential is then of the form

$$V(u_1, u_2, u_3) = V_0 + \frac{1}{2}\alpha_{\perp}(u_1^2 + u_2^2) + \frac{1}{2}\alpha_{\parallel} u_3^2 + \delta(u_1^4 + u_2^4 - 6u_1^2 u_2^2). \quad (9)$$

By following Willis (1969; §4.2), we arrive at the following form for the temperature factor of the X atom:

$$\exp\{-W_X(\mathbf{Q})\} = \exp\left[-Q_{xy}^2 \frac{k_B T}{2\alpha_{\perp}} - Q_z^2 \frac{k_B T}{2\alpha_{\parallel}}\right] \times \{1 - (k_B T)^3 (2\pi/a)^4 (\delta/\alpha_{\perp}^4) \times (h_1^4 + h_2^4 - 6h_1^2 h_2^2)\}, \quad (10)$$

where a is the lattice parameter, k_B the Boltzmann constant, T the absolute temperature, $Q_{xy}^2 = (2\pi/a)^2 (h_1^2 + h_2^2)$, and $Q_z^2 = (2\pi/a)^2 h_3^2$.

Comparison with (2) shows that

$$\beta_{11} = (2\pi^2/a^2) k_B T/\alpha_{\perp}$$

$$\beta_{33} = (2\pi^2/a^2) k_B T/\alpha_{\parallel}$$

and with $\beta_{11} = (44 \pm 2) \times 10^{-4}$, $\beta_{33} = (56 \pm 2) \times 10^{-4}$ and $T = 293$ K,

$$\alpha_{\perp} = 10.3 \times 10^{-19} \text{ J } \text{\AA}^{-2}$$

$$\alpha_{\parallel} = 8.1 \times 10^{-19} \text{ J } \text{\AA}^{-2}.$$

The anisotropic fourth-order term bears a close resemblance to (5) except for the coefficient of $h_1^2 h_2^2$, which is 6 rather than 3. This is then a special case of (4), in which the second- and fourth-order contributions to the potential are separated, and, under these conditions, $\delta = (160 \pm 30) \times 10^{-19} \text{ J } \text{\AA}^{-4}$.

The anharmonic contribution is reduced at low temperature and, using (10) for the temperature factor, we find at 150 K that $\delta \simeq 200 \times 10^{-19} \text{ J } \text{\AA}^{-4}$ so that the reduction of the anharmonic term is approximately as T^3 . Further quantitative examination of this point would require a treatment beyond the classical limit (Dawson, 1970), especially since the Debye temperature for most of these materials is between 200 and 300 K (van Maaren, van Daal & Buschow, 1974), and our model assumes $T > \theta_D$.

By restraining the temperature factor as in (10) we are able to separate the second- and anisotropic fourth-order parts of the potential as shown in (9). To visualize the significance of these parameters we have mapped out the radial dependent part of the potential of (9) in Fig. 9 in the (xz) and (xy) planes. The most striking feature is the softening of the potential in the [110] direction, *i.e.* there is a partially attractive potential in the direction of the U-Ge nearest neighbor. In assessing the significance of these potential maps one should bear in mind not only the approximations discussed above, but also the absolute magnitudes of the atomic displacements. For example, the square root of the mean-squared deviation $\langle u^2 \rangle^{1/2} = 0.065$ \AA, whereas we illustrate the potential out to 0.15 \AA. Nevertheless, our analysis does suggest a softened potential in the U-Ge direction and Fig. 9 is an attempt to represent this qualitatively.

In conclusion, we have shown the presence of both second-order anisotropic and fourth-order terms in the thermal parameters of the X atom in a series of UX_3 systems. We anticipate these effects in other AB_3 systems. Indeed, experiments on $CeSn_3$ (Loong, Stassis & Faber, 1980) have shown that in this interesting compound $\beta_{33}/\beta_{11} \approx 1.60$, *i.e.* larger than the values in Table 2. Preliminary experiments on $AuCu_3$ itself

(Faber, Lander & Brown, 1980) have shown that whereas $\beta_{33}/\beta_{11} \approx 1$, the fourth-order terms are larger than seen in any other system examined. Such an effect may have an important bearing on the microscopic interactions driving the order-disorder transition in $AuCu_3$.

We would like to thank A. J. Arko and J. F. Reddy for providing the samples and R. L. Hitterman for technical assistance. We are grateful to M. Lehmann for advice and help with respect to the experiments at the Institut Laue-Langevin. Discussions with and encouragement from J. B. Cohen are appreciated.

References

- ARKO, A. J., BRODSKY, M. B., CRABTREE, G. W., KARIM, D., KOELLING, D. D., WINDMILLER, L. R. & KETTERSON, J. B. (1975). *Phys. Rev. B*, **12**, 4102-4112.
- ARKO, A. J. & KOELLING, D. D. (1978). *Phys. Rev. B*, **17**, 3104-3114.
- BIRSS, R. R. (1964). *Symmetry and Magnetism*, pp. 54-70. Amsterdam: North-Holland.
- COOPER, M. J., SAKATA, M. & ROUSE, K. D. (1979). *Acta Cryst.* **A35**, 250-251.
- DAWSON, B. (1970). In *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, pp. 101-123. Oxford Univ. Press.
- DELAPALME, A., LANDER, G. H. & BROWN, P. J. (1978). *J. Phys. C*, **11**, 1441-1450.
- FABER, J., LANDER, G. H. & BROWN, P. J. (1980). *Program and Abstracts, Am. Crystallogr. Assoc. Winter Meeting, Eufaula, Alabama*, Vol. 7, No. 2, p. 34.
- JOHNSON, C. K. (1970). In *Thermal Neutron Diffraction*, edited by B. T. M. WILLIS, pp. 132-160. Oxford Univ. Press.
- KOELLING, D. D. (1980). Private communication.
- LANDER, G. H., REDDY, J. F., DELAPALME, A. & BROWN, P. J. (1980). *Phys. Rev. Lett.* **44**, 603-606.
- LOONG, C.-K., STASSIS, C. & FABER, J. (1980). *Program and Abstracts, Am. Crystallogr. Assoc. Winter Meeting, Eufaula, Alabama*, Vol. 7, No. 2, p. 37.
- MAAREN, M. H. VAN, VAN DAAL, H. J. & BUSCHOW, K. H. J. (1974). *Solid State Commun.* **14**, 145-147.
- WILLIS, B. T. M. (1969). *Acta Cryst.* **A25**, 277-300.
- WILLIS, B. T. M. & PRYOR, A. W. (1975). *Thermal Vibrations in Crystallography*, p. 173 *ff.* Cambridge Univ. Press.

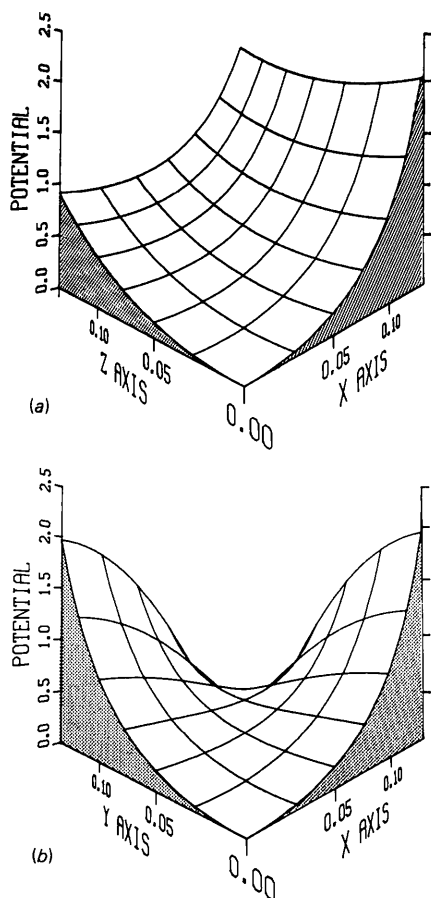


Fig. 9. Schematic representation of the potential function around the Ge atom at room temperature; the units of distance are Å and of potential are arbitrary. The origin of these figures refers to the Ge atom at $(\frac{1}{2}\frac{1}{2}0)$ in Fig. 1; (a) the (xz) plane; and (b) the (xy) plane.