Search for lattice distortions in UN, UAs, and USb at low temperatures

H. W. Knott, G. H. Lander, and M. H. Mueller Argonne National Laboratory, Argonne, Illinois 60439

O. Vogt

Eidgenössische Technische Hochschule, Lab für Festkörperphysik, CH-8093 Zurich, Switzerland (Received 16 July 1979)

Single crystals of UN, UAs, and USb have been examined by x-ray diffraction at low temperatures to measure the lattice parameter and search for lattice distortions associated with the magnetic ordering. We have been unable to find any distortion, implying that the external strain is less than 2×10^{-4} in all three materials. Significant changes in the volume accompany the magnetic ordering and the first-order I–IA transition in UAs. We do, however, observe a small line broadening of the diffraction profile in all three materials as the temperature is lowered. The possible origins of this are discussed.

I. INTRODUCTION

The unusual magnetic properties of the uranium monopnictides have recently been the subject of a number of investigations, which are reviewed in Ref. 1. These materials have rocksalt structure and order antiferromagnetically at relatively high temperatures. One of the most intriguing questions about these materials is whether they exhibit a tetragonal distortion in their ordered state. In this paper we report x-ray measurements aimed at addressing this question. Our results are in a certain sense negative in that distortions are not found. We discuss possible reasons for this; for example, from an experimental point of view the "domain question" is important and, on a more fundamental level, one question is whether the magnetic structures consist of a single \vec{q} component or are multiaxial, i.e., more than one \vec{q} vector. The experiments set an upper limit on the possible tetragonality, $\delta = |c/a - 1|$, remove some confusion from the existing literature, and serve to delineate further the differences between the ferrro- and antiferromagnetic uranium compounds.

To gain some perspective we might look at the lanthanide, 4f series, which, like the actinides, have large orbital moments. Experiments on *both* ferromagnets and antiferromagnets have shown reasonably large distortions, which in some cases can be as great as 1%.^{2,3} As shown by Bak and Lindgard,³ the distortion (or external strain) can be related directly to the crystal-field levels and their associated quadrupole moments.

The first report on the symmetry of uranium samples in their ordered state was given by Marples,⁴ who showed that US, a ferromagnet with rocksalt structure, has a spontaneous distortion beginning at T_C (=178 K) and which at 5 K corresponds to an external strain of 105×10^{-4} . Following this Lander and Mueller⁵ reported investigations of a number of polycrystalline actinide samples. The most important conclusion of this study was that there appears to be a major difference between the ferromagnets, which show very large distortions, and the antiferromagnets, which show almost no distortions at all. Marples⁴ was also unable to observe any tetragonality in polycrystalline samples of UP and UN when they ordered antiferromagnetically. Later, Marples et al.⁶ examined a single crystal of UN and reported a tetragonal distortion of $\delta = -(6.5 \pm 0.3) \times 10^{-4}$. As we shall show, we believe this material distorts much less than this, if at all, and the line broadening observed by Marples et al.⁶ is a result of internal strains.

II. EXPERIMENTAL

The experiments have all been performed on (100) faces of single crystals with the high-angle x-ray diffractometer (Bond) technique. The cryostat is of a conventional design with two beryllium windows through which the x-ray beam can pass. The crystals were fastened with vacuum grease onto a large copper block in a variable-temperature cryostat. Heaters and calibrated platinum and germanium resistors were embedded in the block and temperature control to ± 0.2 K was attained with an exchange-gas system. All measurements were made with a copper target using either the $K\alpha$ or $K\beta$ characteristic lines.

To obtain a quantitative measure of the lattice distortion, we use a least-squares routine to fit a calculated x-ray profile to the experimental intensities.

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The method is identical to that described earlier.⁵ The function used is a Cauchy function so that

 $y_{ij} = \frac{mL_p S}{\Delta} \left/ \left[1 + \left(\frac{2\theta_j - 2\theta_i}{\frac{1}{2}\Delta} \right)^2 \right] , \qquad (1)$

where y_{ij} is the intensity from a reflection $(hkl)_j$ at the position $2\theta_i$, *m* is the multiplicity of the reflection arising from different domains, L_p is the Lorentzpolarization factor, *S* is the scale factor, $2\theta_j$ is the calculated central position of the diffraction peak, and Δ is the full width at half maximum (FWHM) of the diffraction profile. At the position $2\theta_i$, the total intensity is $\sum y_{ij}$, where the sum is over all reflections and incident wavelengths (i.e., the α_1 and α_2 components). We have also tried a Gaussian function to fit the profile but the Lorentzian form appears to be slightly better.

As we shall see, the overall fit is reasonably good, certainly good enough to compare results at different temperatures. A more refined analysis is not justified for diffraction patterns from these types of crystals which can often have a mosaic spread larger than the intrinsic x-ray resolution. One then gets a series of peaks which can only be approximated as a Gaussian. Even with the best crystals this problem may distort the line shape, and the mosaic spread of the individual crystallites may also change as a function of temperature.

A. Domains

The measurements reported here were carried out on single crystals. However, our interpretation and ability to observe a change from cubic to lower symmetry depends on the crystals being multidomain in character. To understand this we can imagine a single crystal ordering magnetically with spins along a cube axis. Since there are three equivalent (100)axes, the single crystal will be made up of domains, each one of which contains magnetic moments in a single direction. If the symmetry of the unit cell is lowered in the ordered state to tetragonal, then within the [001] domain, i.e., $\vec{\mu}$, the magnetic moment, parallel to [001], $d_{001} \neq d_{100}$ where d_{hkl} is the interplanar spacing. In the x-ray experiment if the beam impinges on an area containing two domains, then we will see peaks corresponding to d spacings of d_{001} and d_{100} , thus allowing a deduction of the tetragonality. However, if the beam strikes a single domain a single d spacing is sampled. This may, of course, change in value on going through the transition temperature, but such a change may come from volume effects since $V = d_{100}^2 d_{001}$ in a tetragonal system. In our experiments the x-ray beam size was of the order of 1×1 mm, and the penetration depth is \sim 5 μ m for an attenuation factor of 0.1. These dimensions are the same order of magnitude as expected for the magnetic domains. Indeed, in an experiment⁷ on single crystals of CeBi we have seen the domain effects and demonstrated that by scanning across the surface with the x-ray beam this effect can be identified. In the present experiment we have performed such scans and at no time found evidence for double-peak structures.

These problems associated with domain behavior are not present with polycrystalline samples, but the need to maximize sensitivity by using high-angle reflections makes the experiments difficult because of the resulting low counting rates and overlap of reflections. Experiments^{4,5} on polycrystalline UN and UAs have failed to find any evidence of a tetragonal distortion, $|\delta| \leq 5 \times 10^{-4}$.

III. RESULTS

A. Uranium nitride

Uranium nitride orders antiferromagnetically⁸ at $T_N = 50$ K. The magnetic structure consists of ferromagnetic (001) planes coupled antiferromagnetically in a simple +-+- sequence, the so-called type-I structure. The moments point along the *c* axis, i.e., along the propagation direction of the magnetic structure. (This is the single \vec{q} structure; we shall return later to the implications of a multi- \vec{q} structure.)

A good single crystal of UN proved extremely difficult to find. Finally, a suitable (100) face was polished and the (600) reflection examined with Cu $K\alpha$ at 80 and 5.25 K. At 80 K the FWHM was 0.37° and at 5.25 K the value was 0.40°. The full diffraction peak and the least-squares fit are shown in Fig. 1.



FIG. 1. Diffraction profile of the (600) reflection of UN at 5.25 K taken with Cu $K\alpha$ radiation. The open points are from experiment; the solid lines are the theoretical fit. The double-peak structure arises from the α_1 and α_2 wavelength components and not from a tetragonal distortion.

The volume expansion on cooling in UN is well documented⁶, so that $(V_{50 \text{ K}} - V_{5 \text{ K}})/V_{5 \text{ K}} = -8 \times 10^{-4}$.

The question now arises as to whether the broadening is caused by a tetragonal distortion. Thus for a *small* distortion δ the difference between d_{100} and d_{001} may be less than that resolvable by the instrument. (In practice, the limiting factor is usually not the instrumental resolution, at least with x rays, but more often the intrinsic linewidth from the material.) In this case the observed profile will be slightly broadened. A further increase in δ will lead to an asymmetry of the peak, because d_{001} and d_{100} have different multiplicities, and finally, for large δ , the peaks will be well separated. In an attempt to quantify these statements, we have performed the



FIG. 2. Plots of Δ , the full width at half maximum, FWHM, against δ , the simulated tetragonal distortion. See text for details. The solid lines are parabolic fits to Eq. (2), which only fit for small δ . The different values of Δ_0 (Δ when $\delta = 0$) arise because of crystal mosaic and the differing diffraction angles used.

following analysis. A tetragonal distortion δ was simulated by the superposition of two Lorentzians. The intrinsic half-width of each Lorentzian was Δ_0 , corresponding to the high-temperature *normal* state of the material. For a given δ (small) we then measure Δ , the effective half-width of the combined curve. The results of these computer analyses are illustrated in Fig. 2. For δ small

$$\Delta^2 = \Delta_0^2 + c \,\delta^2 \quad , \tag{2}$$

where c is a constant depending on Δ_0 and the diffractometer angle. The resulting parabolic fits are shown as solid lines in Fig. 2. Obviously as δ increases, Eq. (2) no longer holds and, more importantly, the peaks become asymmetric. Hence the solid lines deviate from the points. Consider the curve for UN starting from $\Delta_0 = 0.37^\circ$, the hightemperature value. If $\Delta_{5 \text{ K}} = 0.40^\circ$, the curve tells us that $\delta(=|c/a-1| \leq 3 \times 10^{-4})$ is the magnitude of a possible tetragonal distortion.

We have performed a similar analysis on the results given by Marples *et al.*⁶ Here $\Delta_0 = 0.25^\circ$, and they claim $|\delta| = 6.5 \times 10^{-4}$. According to Fig. 2, this is outside the parabolic regime, and the profiles *should* show a marked asymmetry (Fig. 3). Marples *et al.*⁶ do not show a diffraction profile in their paper, neither do they comment on any asymmetry. Of course, if *both* a line broadening (i.e., $\Delta > \Delta_0$) and a tetragonal distortion (i.e., $|\delta| > 0$) occur, then they cannot be separated with just one diffraction peak. Marples *et al.*⁶ found the (442) to be much less af-



FIG. 3. Simulated (600) diffraction peak of UN with $\delta = -7 \times 10^{-4}$ and $\Delta_0 = 0.25^{\circ}$. This figure refers to an analysis of the results reported by Marples *et al.* (Ref. 6) (see text for a discussion).

fected than the (600), but the best method is to examine planes of the form (hhh) which are not split by a tetragonal distortion,⁵ and therefore would provide a direct measure of the line broadening. Unfortunately, this argument is weakened if the strains are anisotropic (and we have evidence for such anisotropy), and a technical difficulty exists for these materials in preparing good (111) faces.

B. Uranium arsenide

Uranium arsenide orders antiferromagnetically⁹ at $T_N = 126$ K, with the type-I magnetic structure as in UN. At 63.5 K a first-order phase transition occurs in the type-IA magnetic structure in which the (001) ferromagnetic planes are now coupled in the sequence + + - -, rather than the alternating sequence + - + - of the type I. The moment direction is still along the propagation direction. As shown by Marples *et al.*⁶ with a polycrystalline sample, the thermal-expansion coefficient does not vary at T_N , but the lattice expands at the I \rightarrow IA transition with ($V_{65 \text{ K}} - V_{5 \text{ K}}$)/ $V_{5 \text{ K}} = -4 \times 10^{-4}$.

Our measurements are in excellent agreement with these results. In Fig. 4 is shown an experimental profile with the fitted curve for the (800) reflection taken with Cu $K\beta$ radiation. The lattice parameter and full width at half maximum down to 60 K are shown in Fig. 5. The full width at half maximum steadily increases in the magnetic phase but appears to have no relation with the development of the ordered moment, which sets in very abruptly at 126 K and is almost completely developed by 90 K. The increase in FWHM may be also discussed in terms of a



FIG. 4. Diffraction peak (open points, experiment; solid line, theory) for the (800) reflection from a UAs single crystal taken at 150 K with Cu $K\beta$ radiation.



FIG. 5. Lattice parameter and full width at half maximum for UAs between 60 and 150 K. (Note suppressed zero for FWHM scale.)

tetragonal distortion with the aid of Fig. 2. With $\Delta_0 = 0.386^\circ$, then $\Delta = 0.398^\circ$ corresponds to $|\delta| = 1.5 \times 10^{-4}$. As with the experiments on UN, we find that for $|\delta| > 3 \times 10^{-4}$ the peak shapes are very asymmetric.

The variation in FWHM for UAs as a function of temperature in Fig. 5 appears very large when plotted on this scale. However, it is also instructive to look at the total profile. To do this we have taken the total profile at 57.5 K (in the type-IA state) and subtracted the profile at 150 K (in the paramagnetic state) shown in Fig. 4. The result is shown in Fig. 6. Since the thermal contraction of the support stem in the cryostat results in a small movement of the crystal between these runs, we normalized the integrated intensities before performing this analysis. The total integrated intensity in Fig. 6(a) is therefore zero, but the symmetry about the I = 0 position is sensitive to any difference in peak shapes. In Fig. 6(b) the positive intensity is simply plotted as it appears in Fig. 6(a), but the negative intensity is reversed and plotted



FIG. 6. Differential profile analysis of the UAs results. (a) I(57.5 K) - I(150 K) with the peak positions marked by arrows. (b) Superposition of two portions about the zero-count position. If the peaks were identically the same shape, this superposition would be complete.

as points. The difference between these two is clearly very small. The importance of this analysis is that it is independent of the shape we take for the theoretical fit.

C. Uranium antimonide

Uranium antimonide orders antiferromagnetically¹⁰ at ~ 225 K with the type-I magnetic structure. The first single crystal (now destroyed) we examined ordered at 241 K, but the present crystal was found to order at 220.6 \pm 0.5 K, see Fig. 7. Values for T_N in the literature for USb range from 215 to 240 K, presumably as a result of stoichiometry; so these variations between different crystals are not totally unexpected. The lattice parameter is shown in Fig. 7 (b). The initial thermal-expansion coefficient is ~ 7 × 10⁻⁶/K but directly below T_N the value is - (18 \pm 2) × 10⁻⁶/K so that ($V_{225 \text{ K}} - V_{150 \text{ K}}$)/ $V_{150 \text{ K}} =$ - 21 × 10⁻⁴. At lower temperatures the intrinsic lattice contraction is again evident; the magnetic mo-



FIG. 7. Results for USb: (a) Intensity of the neutron peak at (110) as a function of temperature, giving $T_N = 220.6 \pm 0.5$ K. (b) Lattice parameter as a function of temperature. (c) FWHM, full width at half maximum, as a function of temperature for the (800) reflection measured with Cu K\alpha radiation.

ment is fully developed¹⁰ by ~ 120 K in USb; so below this temperature magnetoelastic interactions are constant and lattice effects produce a small positive thermal expansion.

The variation of the full width at half maximum is shown in Fig. 7(c). Referring to Fig. 2 we see that the distortion $|\delta| < 1.5 \times 10^{-4}$ for this broadening. (Note that in USb the diffraction angle is between 168 and 170° so the sensitivity is considerable.)

IV. DISCUSSION

Our attempts to find, and measure, tetragonal distortions in UN, UAs, and USb have been unsuccessful. We believe such distortions $|c/a-1| < 2 \times 10^{-4}$. This is still a large lower limit by the standards of distortions that lower the symmetry. For example, in chromium strain-gauge measurements on a singledomain state were needed before the distortion of

Material	Structure	a ₀ (Å) at 300 K	<i>Т_с</i> (К)	<i>Т_N</i> (К)	Magnetic	$10^4 \frac{c-a}{c-a}$		
					structure	Distortion	(±3)	Ref
US	NaCl	5.489	178		F	R	+105	a
USe	NaCl	5.75	160		F	R	+ 81	a
UTe	NaCl	6.155	100		F	R	+67	b
NpC	NaCl	5.005	220		F	R	+23	с
NpN	NaCi	4.897	87		F	R	-52	с
PuP	NaCl	5.667	125		F	Т	-31	d
NpFe ₂	Laves	7.144	~500		F	R	-120	d
NpNi ₂	Laves	7.098	32		F	R	43	d
NpP	NaCl	5.615		130	3+,3-	Т	-42	с
NpAs	NaCl	5.838		175	4+,4-	Т	-8	с
UN	NaC1	4.890		53	I		<2	
UP	NaCl	5.589		125	Ι		≤5	а
UAs	NaC1	5.779		127	1 & IA		<2	
USb	NaCl	6.191		220	I		<2	
NpC	NaCl	5.005		310	1 I		≤5	с
NpAs	NaCl	5.838		(142)	I		≤3	с
NpSb	NaCl	6.254		207	I		≤15	с
NpS	NaCl	5.527		20	II		≤3	с
UO ₂	CaF ₂	5.470		31	I		<2	e
NpO ₂	CaF ₂	5.434		24	?		≤3	с

TABLE I. Actinide compounds that have been examined at low temperature by x-ray diffraction for distortions. For a rhombohedral distortion, the change from the rhombohedral angle of 60° is given by $\Delta \alpha = -4/(27)^{1/2}(c-a)/\alpha$ rad, where the distances c and a are measured parallel and perpendicular to the trigonal axis, respectively. In the cubic phase, c/a = 1.00.

^aMarples (Ref. 4).

^bF. Hulliger (private communication).

^cLander and Mueller (Ref. 5).

^dMueller et al. (Ref. 12).

^eJ. Faber and M. H. Mueller (unpublished).

 5×10^{-6} was found.¹¹ The strain-gauge method is inapplicable unless an inbalance can be created in the domain population.

These results again amplify the point⁵ we made in 1974 that there is a major difference between the ferromagnets and antiferromagnets. In Table I we present a more recent version of the table given in our previous paper. We can see immediately that, except for NpAs and NpP, no measurable distortions occur in the antiferromagnetic materials. We do not understand this any more than we did five years ago.

One obvious solution to this dilemma would be to accept the multiple- \vec{q} magnetic structure.^{6,13} This structure may be visualized by folding the three propagation directions (i.e., the three- \vec{q} vectors) into one unit cell. Each atom then has a component of magnetization along three mutually perpendicular axes and the total component in a $\langle 111 \rangle$ direction, although the exact $\langle 111 \rangle$ axis changes from atom to atom. An illustration of the three- \vec{q} structure is given in Ref. 6. Such a structure has been found in a USb_{0.9}Te_{0.1} sample, although this material has a ferromagnetic component at low temperature.¹⁴ The most important experimental facts arguing against a multiaxial structure are (a) the anisotropy in the susceptibility in the ordered state¹⁵ and (b) the unusual anisotropy found in the critical scattering near T_N in all three materials.¹⁶ These observations cannot be resolved with a multi- \vec{q} structure with cubic symmetry. Furthermore, the distortions in NpP and NpAs presumably appear because of the complex q values, 0.333 and 0.25, respectively, rather than because of a change from multi- \vec{q} to single- \vec{q} structures. Very recently in a uniaxial stress measurement¹⁷ on UN, changes were seen in the domain population, again arguing against the multiaxial structure.

In all three materials, we have observed a broadening of the x-ray profile. Such changes in the linewidth may be associated with small tetragonal distortions ($\delta \sim 10^{-4}$) but the unusual temperature dependence of the changes in both UAs and USb suggest they are not coupled directly to the magnetization, which is the primary-order parameter. Changes in the diffraction profile can be related to variation in particle size and/or strain effects, i.e., fluctuations in *d* space. There seems no *a priori* reason to expect changes in particle size. Strain effects are certainly to be expected if a change in symmetry occurs. Indeed, in experiments¹⁸ on UMn₂, which distorts from cubic to monoclinic, and on the ferromagnet¹² PuP, which becomes tetragonal, large variations were found in the linewidths of different lines indicating not only the presence of strain but also that it is anisotropic. But the question remains as to how we are to invoke a strain effect without an appreciable distortion? An associated problem, of course, is quite simply how the large term in the magnetoelastic interaction is prevented from driving a lattice distortion. In the ferromagnets, q = 0, and in NpP and NpAs with q = 0.333 and q = 0.250, respectively, distortions occur, but for type I (q = 1) and type IA $(q = \frac{1}{2})$ the effects, if present at all, are at least an order of magnitude smaller. The discovery of an *internal* distortion¹⁹ in UO_2 seemed to offer a way out of this dilemma,²⁰ and searches were made with x-rays⁷ for such an effect in CeBi at the $I \rightarrow IA$ transition and with neutrons in UAs, but neither was successful.

Finally, we should emphasize the importance of resolving the problems discussed here before we can understand the electronic structure of these materials. We are at present considering whether arguments related to the fluctuation of the lattice parameter, which may be considered as a dynamic Jahn-Teller effect,²¹ can resolve the difficulties, and whether high-resolution neutron experiments, where we can truly see the whole sample, would be worthwhile. Neutron experiments with uniaxial stress are also in progress¹⁷ and will, we hope, add further to our understanding.

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