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Magnetoelastic coupling across the field-induced transition of uranium mononitride

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Uranium mononitride (UN) displays a spin-flop-like transition for magnetic field applied along all principal crystallographic directions just below 60 T. Here, we report on ultrasound and magnetocaloric-effect results for UN in pulsed magnetic fields up to 65 T. The field-induced phase transition causes a discontinuous temperature decrease, indicating a larger magnetic entropy above the transition. Furthermore, we find pronounced anomalies in the acoustic properties, which signals strong spin-lattice interactions. A further anomaly observed at fields slightly above the transition is likely related to the formation of magnetic domains. A model based on the exchange–striction coupling mechanism well reproduces the strong renormalization of the acoustic properties.

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I. INTRODUCTION

Uranium monopnictides, and among them the uranium mononitride (UN) attract strong attention of researchers because of two main reasons. First of all, UN is a very interesting material from a fundamental viewpoint due to its intriguing electronic properties. Over the years, the primary focus of a large number of studies was to disclose the nature of the $5f$ electronic states, which are, most probably, responsible for the unique properties of UN. On one hand, the $5f$ electrons are supposed to be itinerant as suggested by studies of pressure-dependent magnetic properties, inelastic neutron scattering, and photoemission [1–4], supported by numerous band-structure calculations (see, e.g., Refs. [3,5–8]). On the other hand, the large magnetic entropy and magnetic-field-induced spin-flop-like phase transition, observed recently in UN [9,10] support the picture of rather localized magnetic moments. Second, recent studies have suggested that UN can serve as a promising fuel material for the fourth generation of nuclear reactors [6,11–13] raising the interest towards possible applications. This proposal is based on a combination of the high thermal conductivity [14–16], high heavy-ion density [17], and high melting point [18,19].

UN crystallizes in a face-centered-cubic NaCl-type structure [20,21] and displays antiferromagnetic (AFM) order with U moments $M_\parallel = 0.75\mu_B$, aligned along the ⟨100⟩ axes below the Néel temperature $T_N = 51–53$ K [22–26]. Earlier high-field magnetization measurements up to 40 T did not show any anomaly [27]. However, recent experiments up to higher fields revealed a spin-flop-like transition just below 60 T [9,10]. The observed magnetization jump likely originates from a reorientation of part of the U magnetic moments in the applied magnetic field. The transition is accompanied by a large negative longitudinal magnetostriction $\epsilon_{100} \approx -5 \times 10^{-5}$ and $\epsilon_{110} \approx -15 \times 10^{-5}$ for the field applied along the [100] and [110] axes, respectively [10]. The long length changes of the sample suggest strong spin-lattice coupling. The ultrasound technique is known to be a highly sensitive probe of magnetoelastic interactions [28] and has the potential to provide crucial information about this field-induced transition.

Indeed, we find pronounced anomalies in the sound velocity and sound attenuation at the field-induced transition for field applied along the principal crystallographic directions of UN. We also observe further features above the transition which are likely related to the formation of high-field magnetic domains. A model based on the exchange–striction coupling well reproduces the large renormalization of the acoustic properties.

II. EXPERIMENTAL DETAILS

UN single crystals were prepared as described in Ref. [9]. The crystal structure was checked using single-crystal x-ray diffraction. The diffracted intensities were collected at ambient temperature using a four-circle diffractometer (Gemini of Agilent) equipped with a Mo tube and an Atlas CCD detector. The CRYSALIS PRO [29] program was used to index the lattice, refine the unit cell, reduce the data, and perform the absorption correction. The structure refinements were carried out using the program JANA2006 [30]. The crystal structure was solved in the space-group $Fm-3m$ (type NaCl) and the final refined lattice constant was found to be $a = 4.887(7)$ Å. Backscattered Laue diffraction was used to check the single-crystalline

*Deceased.
state and to orient the crystals for ultrasound, magnetocaloric effect, and magnetization measurements.

The field and temperature dependences of the relative sound-velocity, $\Delta v/v$, and sound-attenuation, $\Delta \alpha$, changes were measured using a phase-sensitive pulse-echo technique [28,31] in zero and in pulsed magnetic fields up to 65 T. A pair of piezoelectric transducers was glued to opposite surfaces of the sample in order to excite and detect acoustic waves. We measured the longitudinal $C_{11}$ ($k||u||[100]$), $C_{1110} = \frac{1}{3}(C_{11} + C_{12} + 2C_{44})$ ($k||u||[110]$), and transverse $C_{44}$ ($k||[110], u||[100]$) elastic moduli. Here, $k$ and $u$ are the wave vector and polarization of the acoustic waves, respectively. The room-temperature absolute values of sound velocity for these acoustic modes, $v_{11} = [5390 \pm 200]$ m/s, $v_{1110} = [4780 \pm 200]$ m/s, and $v_{44} = [2270 \pm 100]$ m/s, are in good agreement with literature [32–34] when estimated using the relation $v = \sqrt{C/\rho}$, where $\rho = 14.32 \times 10^3$ kg/m$^3$ is the mass density of UN [17,32,33]. The ultrasound frequencies varied between 109 and 130 MHz in our experiments.

III. RESULTS

The crystal lattice of uranium mononitride is strongly coupled to the magnetic degrees of freedom as seen from a pronounced jump of $\Delta v/v$ at $T_N = 51$ K [Fig. 1(a)]. This result is in good agreement with previous elastic-modulus measurements [33,34]. UN probably displays a tiny tetragonal distortion, $c/a = 0.99935$ [37,38], below $T_N$ that, however, cannot explain the large changes in $\Delta v/v$ observed in experiment. We, therefore, assume that the jump-like anomaly of $\Delta v/v$ has a magnetic origin. The lattice hardening below $T_N$ evidently relates to the antiferromagnetic order.

The phase transition into the AFM state also leads to significant anomalies in the sound attenuation [Fig. 1(b)]. As the temperature decreases, $\Delta \alpha$ grows substantially at $T_N$ for longitudinal acoustic waves. Although a single sharp anomaly is observed for the acoustic mode $C_{1110}$ at $T_N$, an additional kink emerges for $C_{11}$ at 44 K. Note that the thermal-expansion coefficient shows an anomaly at about the same temperature as well [10]. The origin of this anomaly is not clear yet. For the transverse acoustic waves ($C_{44}$), $\Delta \alpha$ exhibits a minimum at $T_N$.

The observed strong spin-strain coupling in uranium mononitride suggests that anomalies in ultrasound can be expected in the applied field as well. Below, we concentrate on the magnetic and elastic properties of UN in high magnetic fields.

At 2 K, the magnetization, $M$, displays a spin-flop-like transition at 57.8, 57.3, and 53 T for the field applied along the [100], [110], and [111] axes, respectively [Figs. 2(a)–2(c)]. The transitions are accompanied by a pronounced softening for both longitudinal and transverse acoustic modes [Figs. 2(d)–2(f)]. We observe the largest effect, $\approx 1\%$, when the field is applied along the [100] direction. The sound attenuation shows large peaks at the transitions, specifically for the longitudinal acoustic waves [Figs. 2(g)–2(i)]. For $H//[100]$, $\Delta \alpha$ even exceeds 150 dB/cm.

A broad hysteresis was also detected below approximately 15 T when the field was applied along the [110] and [111] axes [Figs. 2(e), 2(f) 2(h), and 2(i)]. This correlates with magnetostriction results and likely originates from a rearrangement of magnetic domains [10].
An earlier high-field study showed that the critical field and the magnetization jump at the field-induced transition decreased monotonously upon approaching \( T_N \) [9]. Upon increasing temperature towards \( T_N \), our pulsed-field ultrasound experiments reveal unexpected features. For longitudinal acoustic waves \( \Delta v/v(H) \) shows the largest softening followed by a jump of several percent at temperatures between 25 and 40 K [Figs. 3(a)–3(c)]. In the same temperature range, the large peak in \( \Delta\alpha \) changes to a much smaller anomaly for \( H \parallel [100] \) and \( H \parallel [110] \) [Figs. 3(d) and 3(e)]. By contrast, for \( H \parallel [111] \), \( \Delta\alpha \) displays anomalies of comparable magnitude at all temperatures below \( T_N \) [Fig. 3(f)].

Above 2 K, the field dependences of the sound velocity show an additional steplike hardening just above the spin flop for \( H \parallel [100] \) and \( H \parallel [110] \) [Figs. 3(a) and 3(b)]. Note that the magnetization exhibits a tiny anomaly just above the spin-flop transition too [the inset in Fig. 2(b)]. With increasing temperature, the minimum in \( \Delta v/v \) becomes small in comparison with the steplike anomaly. The sound attenuation also shows features at the same fields as the anomalies seen in \( \Delta v/v \) [Figs. 3(d) and 3(e)].

The double anomalies emerge in \( \Delta v/v(H) \) above 2 K for transverse acoustic waves as well. These anomalies are evident in \( \Delta v/v \) and \( \Delta\alpha \) for \( H \parallel [100] \) and \( H \parallel [110] \) [Figs. 4(a), 4(b) 4(d), and 4(e)]. For \( H \parallel [111] \), even a more complex fine structure can be resolved in the vicinity of the spin flop, e.g., for the field sweep at 35 K [Figs. 4(c) and 4(f)]. Pronounced spin-lattice effects were also found in high magnetic fields for another actinide antiferromagnet, \( \text{UO}_2 \) [39].

Our high-field \( \Delta v/v \) and \( \Delta\alpha \) data allow us to estimate the characteristic relaxation time, \( \tau \), related to the spin flop. We use the Landau-Khalatnikov relation,

\[
\tau = \frac{v}{\omega^2} \left( \frac{\Delta\alpha}{\tau} \right),
\]

where \( \omega \) is the angular frequency [28]. Strictly speaking, Eq. (1) is valid for \( \omega \tau \ll 1 \). However, it still gives an approximate value of \( \tau \) unless \( \omega \tau \gg 1 \) [40].

Our estimates show that, for the acoustic mode \( C_{44} \parallel [110] \), \( \tau \) decreases from \( \sim 10^{-5} \) s (\( \omega \tau \approx 3 \)) to \( \sim 10^{-7} \) s (\( \omega \tau \approx 0.3 \)) in the vicinity of 30 K with temperature and field applied along the \([100] \) and \([110] \) directions. This is the temperature region where the large peak in \( \Delta\alpha \) changes to much smaller anomalies [see Figs. 3(d) and 3(e)]. The relaxation time associated with the additional anomaly that emerges at elevated temperatures is \( \sim 10^{-9} \) s (\( \omega \tau \approx 0.3 \)) for both field directions. For the field applied along the \([111] \) axis, the peak in \( \Delta\alpha \) at the spin-flop transition decreases gradually with temperature, and the corresponding relaxation time also changes gradually from \( \sim 10^{-8} \) s (\( \omega \tau \approx 8 \)) at low temperatures to \( \sim 10^{-9} \) s (\( \omega \tau \approx 0.8 \)) at higher temperatures.

For the acoustic mode \( C_{44} \), we could estimate the relaxation time at the anomaly observed in \( \Delta\alpha \) below 30 K. For \( H \parallel [100] \), \( \tau \) increases from \( \sim 10^{-10} \) s (\( \omega \tau \approx 0.2 \)) at 2 K to \( \sim 10^{-9} \) s (\( \omega \tau \approx 2 \)) at 30 K. For \( H \parallel [110] \) and \( H \parallel [111] \), the relaxation time is almost constant \( \tau \sim 10^{-9} \) s (\( \omega \tau \approx 1 \)) between 2 and 30 K.

For both acoustic modes \( C_{44} \parallel [110] \) and \( C_{44} \), the estimated relaxation time is relatively long and characteristic of spin fluctuations.

Figure 5(a) shows the temperature of the sample as a function of field applied along the \([110] \) axis under adiabatic conditions. Initially, the temperature increases presumably...
due to eddy currents and, possibly, domain reorientation, and then levels off. The spin flop causes the temperature to decrease discontinuously by 1 K, indicating that the magnetic entropy above the transition is larger. A small hysteresis is observed here as appropriate for a first-order phase transition.

The change in the entropy, \( \Delta S \), associated with the phase transition, can be estimated using the Clausius-Clapeyron relation [41],

\[
\Delta S = - \Delta M \left( \frac{dH_c}{dT_c} \right).
\]

Here, the slope of the phase boundary, \( dH_c/dT_c \), is obtained from the phase diagram shown in Fig. 6, and the magnetization jump, \( \Delta M \), is taken from a previous high-field magnetization study [9]. \( \Delta S \) at zero field is obtained using the specific-heat data around \( T_N \) [10]. The associated entropy change is 0.4 J mol\(^{-1}\) K\(^{-1}\) at 51 K and decreases to about 0.15 J mol\(^{-1}\) K\(^{-1}\) at 10 K [Fig. 5(b)] as a result of the AFM ordering.

The \( H-T \) phase diagram of UN (Fig. 6) resembles those reported in Refs. [9,10]. The low-field line below about 10 T likely reflects domain reorientation. A spin flop occurs just below 60 T. Previous magnetization and magnetostriction experiments showed single broad anomalies due to the spin flop at elevated temperatures, whereas our ultrasound measurements revealed additional features related to another field-induced transition. These features are presented as two lines in the high-field part of the phase diagram.

Earlier, the existence of a tricritical point was reported in the phase diagram of UN at \( T_{\text{tri}} = 24 \) K and \( \mu_0H_{\text{tri}} = 52 \) T [10]. Our results do not allow us to identify this point unambiguously in the phase diagram shown in Fig. 6. On one hand, we observe hysteresis in \( \Delta v/v \) and \( \Delta \alpha \) at the field-induced transition below as well as above 24 K. On the other hand, the magnitude of the anomaly in \( \Delta \alpha \) vs \( H \) strongly reduces above 30 K for the longitudinal acoustic mode \( C_{L[110]} \) and the field applied along the [100] and [110] axes [Figs. 3(d) and 3(e)]. According to our analysis, this happens due to a decrease in the relaxation time of spin fluctuations. The large changes in \( \Delta \alpha \) might suggest a change in the type of the transition near 30 K, i.e., from the first to the second order, which is in line with the existence of the tricritical point.

### IV. DISCUSSION

The dual nature of the 5f electrons was considered in the so-called dual-nature model [42–46] with competing localized and delocalized 5f electrons for both exact and perturbative theoretical approaches. Our results support this picture. Comparing the Pauli magnetization with our data, the dual nature of the 5f electrons of U can be seen, for example, in Fig. 2(c). Here, we show a calculated contribution of the itinerant electrons to the low-temperature magnetization of UN. The magnetic susceptibility of the conduction electrons (assumed to be noninteracting in our estimates) was obtained from the value of the Sommerfeld coefficient \( 0.045 \) J mol\(^{-1}\) K\(^{-2}\), extracted from the temperature dependence of the specific heat [9]. Evidently, the contribution from the conduction electrons is essential in UN. On the other hand, itinerant electrons themselves cannot explain the observed spin-flop-like phase transition, which is related to the localized magnetic moments (see below).

The renormalization of the sound velocities and attenuation in magnetic systems is caused mostly by two factors [28]. First, sound waves change the ligand (nonmagnetic ions surrounding the magnetic ones) positions, and, therefore, the crystalline electric field (CEF) of the ligands is affected. Due to the strong spin-orbit interaction, the CEF yields changes in the single-ion magnetic anisotropy of the magnetic ions. It also changes the effective \( g \) factors of the magnetic ions. Hence, due to magnetoelastic coupling, sound waves can change slightly the direction of the magnetic anisotropy, and vice versa, the magnetic anisotropy modifies the acoustic
properties, such as the sound velocity and attenuation. This effect has a relativistic nature, and the interaction between the sound wave and the magnetic material properties exists at any temperature lower than the characteristic energy of the single-ion magnetic anisotropy.

Second, sound waves change the positions of magnetic ions and the positions of nonmagnetic ions involved in the indirect exchange coupling (superexchange [47]). In this case, sound waves renormalize the effective exchange interactions between magnetic ions. Typically, this effect is more pronounced than strain-single-ion coupling since the interionic exchange interactions determine predominantly magnetic phase transitions in ordered magnets. Hence, here, we consider such an exchange-striction mechanism to describe our experimental observations.

According to Ref. [48], the exchange-striction coupling in magnetic systems yields a renormalization of the velocity of the sound wave, proportional to some spin-spin correlation functions. These correlation functions can be approximated by a combination of the magnetization and the magnetic susceptibility of the system. References [49–51] present good agreements between experiments and theory for many magnetic systems even if only the homogeneous part of the magnetic susceptibility is taken into account. The renormalization of the sound-velocity, $v$, due to the exchange-striction coupling in the general case can be written as

$$\frac{\Delta v}{v} \approx -\frac{v}{\rho V \alpha^2 \mu^2} \lbrack (g(0))^2 (2M^2 \chi + T \chi^2) + h(0) \mu^2 (M^2 + T \chi) \rbrack,$$

where $V$ is the volume of the crystal, $\mu$ is the effective magneton per magnetic ion, and $\chi$ is the magnetic susceptibility. The magnetoelastic coefficients are

$$h = \sum_j e^{i \mathbf{q} \cdot \mathbf{R}_j} [1 - \cos(k \mathbf{R}_{ji})] (\mathbf{u}_k \cdot \mathbf{u}_k) \frac{\partial^2 J_{ij}^{\beta, \beta'}}{\partial \mathbf{R}_i \partial \mathbf{R}_j},$$

$$g = \sum_j e^{i \mathbf{q} \cdot \mathbf{R}_j} (e^{i \mathbf{q} \cdot \mathbf{R}_j} - 1) \mathbf{u}_k \frac{\partial^2 J_{ij}^{\beta, \beta'}}{\partial R_i} \frac{\partial^2 J_{ij}^{\beta, \beta'}}{\partial R_j},$$

(taken at $\mathbf{q} = 0$), where $\mathbf{R}_{ji} = \mathbf{R}_j - \mathbf{R}_i$, $\mathbf{R}_j$ is the position vector of the $j$th site of the magnetic ion and $J_{ij}^{\beta, \beta'} (\beta, \beta' = x, y, z)$ are the exchange couplings between magnetic ions on the $i$th and $j$th sites. Similar results can be obtained for the sound attenuation,

$$\Delta \alpha \approx \frac{\gamma}{\rho V \alpha^2 (\alpha^2 + \gamma^2)} \lbrack (g(0))^2 (2M^2 \chi + T \chi^2) + h(0) \mu^2 (M^2 + T \chi) \rbrack,$$

where $\gamma$ is the effective relaxation rate. The results of calculations, which use the exchange-striction model, are presented in Figs. 7 and 8 for the renormalization of the sound velocity and attenuation in UN at 2 and 20 K, respectively. Excellent qualitative agreement of the results with the data of our experiments, presented in Figs. 2–4, is found. The difference between the longitudinal $C_{\perp[101]}$ and transverse mode $C_{\perp[110]}$ is determined by the relatively large contribution from the magnetoelastic coefficient $g$ [Eq. (4)] for the longitudinal modes, although $h$ dominates for the transverse modes.

The exchange-striction model correctly reproduces the main acoustic features at the critical field. Calculations for higher temperatures show a broadening of the anomaly with a transformation from first- to second-order phase transition at elevated temperatures. This is a characteristic feature of Ising magnetic systems (with the magnetic-anisotropy energy being of the same order as the exchange interactions) with metamagnetically phase transitions [52].

For $T \sim T_N$ or higher, our calculations do not reveal any anomalies in the magnetoacoustic properties (not shown): They reproduce the monotonic behavior observed in experiments. In addition, we see that the smaller features at about 2 to 3 T and above the spin-flop phase transition are also reproduced (Fig. 8). The missing fine structure above the spin-flop transition for the 2 K data might be masked by the strong anomaly at the spin-flop transition itself. On the other hand, a possible structural distortion for $T < T_N$ [37,38] can enhance these features just below $T_N$. The discrepancies
between the calculated and the experimental results (e.g., the larger changes in the acoustic properties below the spin-flop transition, cf. Figs. 2 and 7) are probably related to the dropped contribution of the inhomogeneous magnetic susceptibility in our calculations.

Now, let us discuss the nature of the observed fine structure in the magnetoacoustic properties. Two possible scenarios can be considered. First, in the Ising layered model used in Ref. [9], the transformation from the AFM to the spin-flop phase might happen via two phase transitions: AFM → $f_{12} → f_{6}$ in notations of Ref. [9].

Another possibility would be an intermediate state (see, e.g., Ref. [53] and references therein). For example, similar features have been observed for the sound velocity in PrFe$_3$(BO$_3$)$_4$ above the spin-flop transition [54]. The intermediate state for magnetic fields larger than the critical field of the spin-flop or metamagnetic phase transition [55] is related to the instability of this phase with respect to the onset of magnetic domains. Magnetic domains with magnetic moments directed along [100] and equivalent [010] and [001], having similar energies, open the possibility for domain formation. In a magnetic sample, the domain structure appears because the magnetization tends to be parallel to the surface, whereas in the bulk of the sample the “easy-axis” magnetic anisotropy determines the direction of the magnetization. Obviously, in antiferromagnets, a nonzero magnetization exists only for fields larger than the critical field of the spin-flop transition.

To summarize, we have performed ultrasound and magnetocaloric-effect measurements of uranium mononitride. The MCE data reveal a discontinuous decrease in the temperature at the spin-flop-like transition, evidencing a larger magnetic entropy above the transition. We have also observed a large renormalization of the sound velocity and sound attenuation of longitudinal and transverse acoustic waves. The pronounced anomalies in $\Delta v/v$ and $\Delta T$ can be explained using a model based on the exchange-striction coupling mechanism. Just above the field-induced transition, our measurements have revealed additional features that are likely related to the formation of magnetic domains.

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[55] It is usually accepted that, for the metamagnetic type of a field-induced first-order phase transition, the energy of the easy-axis magnetic anisotropy is on the same order as the exchange energy, such as in Ising antiferromagnets, whereas, for the spin-flop type, the energy of the anisotropy is much smaller than the exchange energy.