Phonon-induced quadrupolar ordering of the magnetic superconductor TmNi$_2$B$_2$C

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We present synchrotron x-ray diffraction studies revealing that the lattice of thulium borocarbide is distorted below $T_Q \simeq 13.5$ K at zero field. $T_Q$ increases and the amplitude of the displacements is drastically enhanced, by a factor of 10 at 60 kOe, when a magnetic field is applied along [100]. The distortion occurs at the same wave vector as the antiferromagnetic ordering induced by the $a$-axis field. A model is presented that accounts for the properties of the quadrupolar phase and explains the peculiar behavior of the antiferromagnetic ordering previously observed in this compound.

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More than ten years ago it was discovered that four of the rare-earth borocarbides (Tm, Ho, Er, Dy) shows coexistence of superconductivity and antiferromagnetic ordering with comparable transition temperatures $T_c$. Superconductivity occurs below $T_c = 11$ K and the Néel temperature is $T_N = 1.52$ K in TmNi$_2$B$_2$C. The characterization and the understanding of these intermetallic compounds have made much progress during the passed decade, see the recent review [4]. Although unusual phenomena have been detected, the type-II superconductivity of these materials seems to be described by the BCS-theory. The electronic system strongly influences the acoustic and optical $\Delta_4$-phonon branches close to $(0.5, 0, 0)$ and $(0, 0.5, 0)$ in the non-magnetic Lu and Y versions of these compounds [5, 6, 7]. The two vectors connect parallel areas of the Fermi surface [8], so nesting explains why the electron–phonon interaction is particularly large at these wave vectors. This enhancement of the electron–phonon interaction is probably the primary reason for the relatively high $T_c$-values of the borocarbides. Nesting is generally also assumed to be important for the magnetic susceptibility of the band electrons by causing a maximum in the Ruderman–Kittel–Kasuya–Yoshida (RKKY) coupling of the rare-earth moments at the nesting vectors [8].

The magnetic properties of TmNi$_2$B$_2$C single crystals have been studied by magnetization measurements [9] and by neutron diffraction [10, 11, 12]. The ordering vector at zero field is $Q_F = (0.094, 0.094, 0)$ with the magnetic moments transversely polarized along the easy $c$ axis. The shift of the magnetic ordering vector away from zero is probably a consequence of the Anderson-Suhl screening of the long-wavelength susceptibility of the superconducting electrons [11]. Applying a field in excess of 10-15 kOe along [100], the magnetic ordering changes into another antiferromagnetic one at the wave vector $Q_A = (0.483, 0, 0)$. The new magnetic phase was considered to be the stable one at zero field in case the electrons were normal, but because the superconducting electrons were more strongly affected by the superzone energy gaps at $Q_A$ than at $Q_F$, the long-wavelength ordering would become the most favorable one of the combined system at small fields. In the original experiment only fields of up to 18 kOe were applied. The extension of the experiment up to a field of 60 kOe clearly showed that this conjecture could not be correct, since the $Q_A$-phase becomes the more stable the higher the field is, and the temperature variation more and more resembles that of the antiferromagnetic order being induced by the uniform field. This highly surprising observation motivated our search for a field-dependent quadrupolar ordering of the system, observable through the accompanying deformation of the lattice.

The experiments were performed at HASYLAB using the BW5 high-energy ($\approx 100$ keV) beam-line with a triple-axis diffractometer and (1,1,1) Si/Ge-gradient crystals as monochromator and analyzer. The single crystal of TmNi$_2$B$_2$C, grown by the flux-method [12], is plate-like with irregular plate-shape and approximate dimensions $4 \times 4 \times 0.8$ mm$^3$ along the $a$, $b$ and $c$ axes, respectively. The crystal was mounted with the $a$ and $c$ axes in the scattering plane of a horizontal 10 tesla cryo-magnet. Geometric constraints required that the field was offset by $5^\circ$ from the $a$ axis in order to probe the expected lattice distortion wave with the symmetry of the $\Delta_4$-phonon mode close to $(0.48, 0, 8)$ along with the (0,0,8) Bragg reflection. Temperature and field dependent superstructure peaks were found at scattering vector (0.484(2),0,8) with the integrated x-ray intensities as shown in Fig. 1. In order to include the intensity from minor satellite crystallites we use numerical summation. The x-ray cross-section is completely dominated by the scattering from the Tm ions, and scans performed at (0.484,0,0) showed negligible intensity. This is clear evi-
dence for a transverse displacement of the Tm-ions along the c axis corresponding to the acoustic $\Delta_4$-phonon symmetry. The (0,0,8) Bragg reflection was used as reference for accurate determination of the superstructure peak position and estimates of the superstructure displacement amplitudes. However, the irregular crystal geometry and the small scattering angles result in rather low and uncertain sample transmission coefficients of the order of $4.6 \times 10^{-3}$ and $8.0 \times 10^{-3}$ for the (0,0,8) and (0.484,0,8) reflections, respectively. Including these corrections and defining the strain of the Tm ion at site $R_i$

$$E_{13}(i) = \frac{a_3(R_i)}{a/2} = E_{13} \cos(Q_A \cdot R_i + \phi), \quad (1)$$

we find that the absolute displacements of the Tm ions at 1.7 K and 60 kOe, correspond to a strain amplitude $E_{13} \approx 6 \times 10^{-3}$. The resolution of the diffractometer was determined by the peak profiles of the (0,0,8) Bragg peak yielding a crystal mosaicity of $\approx 0.02^\circ$ FWHM. The scans along the a axis were essentially rocking curves with Lorentzian profiles while scans along c were Gaussian shaped. At low temperatures the correlation length along a, corrected for instrumental resolution, is determined to be 185 Å when the quadrupolar phase coexists with the magnetic $Q_A$ phase, and it attains an almost constant value of $\approx 275$ Å in the $Q_A$ phase. At zero field and low temperatures the Gaussian peaks in the c direction indicate box-like structures of lengths $\approx 230$ Å that increases to values above the resolution limit of $\approx 300$ Å at 100 kOe. The superstructure peak widths are essentially temperature independent at low temperatures but start to broaden when approaching $T_Q$.

Setting up a model we use the crystal-field (CF) parameters of the Tm ions determined from the observation of CF transitions [13] and from the high-temperature susceptibilities [8]. Here we take into account the anisotropy due to the classical dipole–dipole interaction, $J_{aa}(0) = J_{cc}(0) + 9.15$ µeV, adjust the CF-parameters accordingly ($B_{2}^2 = -0.1, B_0^2 = 0.00033, B_1^2 = -0.01, B_3^2 = 0.78 \times 10^{-5}$ and $B_4^2 = -1.1 \times 10^{-4}$ in units of meV) and include the demagnetization field in the Zeeman term.

The zero-field value of $T_Q$ determines the effective two-ion coupling to be $\delta_{cc}(Q_F) \approx 8.7$ µeV, which is also approximately its value at zero wave vector in the normal phase. The purely magnetic part of the Hamiltonian is well characterized, and the additional quadrupolar/magnetoelastic part of the mean-field Hamiltonian is, by symmetry, considered to be

$$\Delta F(i) = -B_{13} E_{13}(i) O_{13}^0(i) + c_E E_{13}^2(i) + \frac{3}{2} B_E E_{13}^4(i)$$

$$- K(Q_A) \left( O_{13}^2(i) + \frac{3}{2} (2O_{13}^2(i) - O_{13}^4(i)) \right). \quad (2)$$

Here $O_{13}^2(i) = \frac{1}{2}(J_x J_z + J_y J_z)$, with $x, y,$ and $z$ along [100], [010], and [001] respectively. $E_{13}(i)$ is determined by minimizing the strain-dependent part of the average free energy:

$$\Delta F = -B_{13} E_{13} \langle (O_{13}^2) \rangle + \frac{3}{2} c_E E_{13}^2 + \frac{3}{2} B_E E_{13}^4$$

where $\langle (O_{13}^2) \rangle$ is the thermal value $\langle O_{13}^2(i) \rangle \cos(Q_A \cdot R_i + \phi)$ averaged over the lattice. $E_{13}$ determines $E_{13}(i)$ according to eq. (1). The transition temperature $T_Q$ of the

**FIG. 1:** The integrated x-ray scattering intensity at (0.484,0,8) as a function of temperature in the presence of an applied field along [100]. The colored symbols used for the different values of the field (in units of kOe) are specified in the legend box. The two figures include the same results, but the intensity scales differ by a factor of 10. The intensity is proportional to the square of the displacement of the Tm ions, and the solid curves show the results derived from the model. The insert shows the field dependence of the strain amplitude $E_{13}$ at 1.7 K derived from the experiments in comparison with the calculated results.
quadrupolar ordered phase is independent of the value of the fourth-order elastic constant \( B_E \). It is determined by the effective quadrupolar coupling

\[
K_{\text{eff}}(Q_A) = K(Q_A) + \frac{B^2_A}{2c_E}
\]

being equal to the inverse of the non-interacting quadrupolar susceptibility at the temperature \( T_Q \), or \( K_{\text{eff}}(Q_A) = 1/\chi_{Q_A}(T_Q) = 0.0187 \text{ meV} \), when assuming \( T_Q = 13.5 \text{ K} \) at zero field. The properties of the CF Hamiltonian imply that the quadrupolar susceptibility increases with the \( \alpha \)-axis field, and the predicted field dependence of \( T_Q \) is in reasonable agreement with observations according to Fig. 1. In the zero-temperature limit \( \chi_{O_{2}^{1}} \) becomes even more sensitive to the field. Here its maximum value at a field of 20 kOe is nearly a factor of 3 larger than the zero-field value. Although this increase is large, it is far from explaining the dramatic enhancement of \( E_{13} \) observed at 1.7 K, see the insert of Fig. 11. In the non-magnetic borocarbides, the electron–phonon interaction is close to enforce a complete softening of the \( \Delta_q \)-phonon mode at the nesting wave vector corresponding to \( Q_A \) in the Tm system. The phonon energy is 10 meV at room temperature and about 4 meV at 4.2 K in the Lu compound [8]. In the model above, the effects of the electron–phonon interaction are included in terms of the phenomenological parameters \( c_E \) and \( B_E \). If the electron–phonon interaction is as important in the present system as in Lu borocarbide, then \( c_E \) should be small, nearly zero, and \( B_E \) would be decisive as soon as the lattice distortion becomes non-zero. This is the argument for introducing \( B_E \), which has the additional effect that the two contributions to the effective quadrupolar coupling behave differently. This allows a differentiation between the effects due to \( B_{13} \) and those due to the quadrupolar–quadrupolar interaction \( K(Q_A) \).

The quadrupolar ordering has the unique consequence (we are not aware of any other systems showing this behavior) that the application of a uniform field induces a modulated magnetic moment perpendicular to the field. This effect was the very reason why we started to look for the quadrupolar ordering, and the explanation for it is straightforward. When \( E_{13}(i) \) or \( \langle O_{2}^{1}(i) \rangle \) is non-zero, the CF Hamiltonian includes an anisotropy term \( O_{2}^{1}(i) \). This implies that the paramagnetic moment of the \( i \)th site induced by an \( x \)-axis field is not along the field, but is rotated an angle towards the \( z \) axis in proportion to the size of the anisotropy term. Since the anisotropy, proportional to \( O_{2}^{1}(i) \), is modulated in a sinusoidally way with the wave vector \( Q_A \), the \( z \) component of the induced moment is going to show the same modulation. The tetragonal symmetry of the system implies that the Hamiltonian also includes the equivalent terms obtained by interchanging \( x \) and \( y \) in eq. 2. In the domains in which \( \langle O_{2}^{1}(i) \rangle \) is ordered with the wave vector \( Q_A = (0, 0.484, 0) \), the application of a field along \( [100] \) does not produce any perpendicular magnetic component, and the quadrupolar order parameter is only weakly changed by the field. This means that the \( [100] \) field induces a modulated \( z \)-axis moment at the wave vector \( Q_A \) but not at \( Q_A' \), and it destabilizes the \( Q_A' \) domains. Hence, the first circumstance explains the absence of magnetic scattering peaks at \( \pm Q_A' \) discussed in Refs. [11, 12]. In the final comparison between the model and the experiments, we have introduced one more parameter, namely, the value of \( J_{\alpha}(Q_A) \). This parameter is not decisive for the magnitude of \( \langle J_{\alpha}(Q_A) \rangle \) (notice that \( T_Q \gg T_N \)), but is important for \( E_{13} \) at the lowest temperatures, and the fit is significantly improved, when assuming this parameter to be small or, actually, slightly negative. The final model is

\[
|B_{13}| = 1.91, \quad c_E = 360, \quad B_E = 4.8 \times 10^7 \\
K(Q_A) = 0.0086, \quad \langle J_{\alpha}(Q_A) \rangle = 0.0029
\]

all in units of meV. The different quantities have been calculated, see Ref. 14, by assuming a commensurable quadrupolar ordering with a period of 25 lattice planes along the \( \alpha \) axis, i.e. \( Q_A \equiv (0.48, 0, 0) \). The square of the distortions is observed to be a factor of 2–3 smaller than calculated at fields below 15 kOe. An equal population of the \( Q_A \)- and \( Q_A' \)-domains, at the lowest values of the

![FIG. 2: The temperature dependence of the integrated neutron scattering intensity at \( Q_A = (0.484, 0, 0) \) at various values of the applied field along \( [100] \), see Ref. 12. The different values of the field (in units of kOe) are specified in the box. The results were obtained in two different experimental set ups (circles and squares). The repetition of the experiment at 40 kOe was used for determining a common scale for the two sets. The intensity is proportional to the squared amplitude of the transverse magnetic moment at the wave vector \( Q_A \) and the solid lines are the calculated results.](image)
field, may account for a factor of 2. The model neglects any direct consequences of superconductivity on the magnetic phase diagram, but the experimental x-ray scattering intensities show kinks in their temperature variations at the points where the field is equal to the superconducting critical field \( H_{c2} \). This indicates a (moderate) reduction of the quadrupolar order parameter in the superconducting phase.

The neutron-diffraction results \[12\] are compared with theory in Fig. 2 assuming that the value 6 on the intensity scale corresponds to the moment amplitude of 5.0 \( \mu_B \). The calculated amplitudes of the modulation of the moments are of the right order of magnitude. The maximum of the amplitude in the zero-temperature limit is predicted to occur as soon as the system leaves the \( Q_F \)-phase, at a calculated field of 17 kOe to be compared with an experimental value of 10-15 kOe. The experimental maximum is at about 40 kOe, but we have to remark that there are relatively large, unexplained scatter in the experimental results. Instead of focusing on the discrepancies we rather emphasize the ability of the present model to account for the highly disparate variation of the properties of the system. Using a simple elastic model we estimate that \( c_E = 360 \text{ meV} \) corresponds to an acoustic phonon mode at 2.4 meV close to the soft phonon energy of 4 meV observed in the Lu compound. The value of \( B_E \) also appears to be acceptable. The entropy of the electron–phonon system has nearly vanished and the electron–phonon parameters \( c_E \) and \( B_E \) are expected, as assumed, to stay practically constant below 20 K. Because of the small non-magnetic entropy, the heat capacity anomaly at \( T_Q \) is expected to be weak, since the CF contribution of the 4f electrons is negligible (the ground-state doublet remains degenerate at zero field).

The analysis indicates that the electron–phonon system in \( \text{TmNi}_2\text{B}_2\text{C} \), like in the Lu compound, is very close to the point of a lattice instability. In \( \text{TmNi}_2\text{B}_2\text{C} \), the transition is occurring because of the additional contributions of magnetoelastic and quadrupolar–quadrupolar interactions. The magnetoelastic interaction derives from the electrical crystal field produced by the displacements of the ions, whereas the quadrupolar–quadrupolar interaction may be mediated by the same charge-density wave responsible for the strong electron–phonon interaction, and, hence, may be an additional consequence of the Fermi-surface nesting. One of the surprises of the present analysis is that the RKKY-exchange interaction does not seem to be much influenced by the nesting, since the interaction is found to be much smaller at the nesting wave vector than at \( Q_F \).

In conclusion, the x-ray experiments exposed the presence of a quadrupolar phase in \( \text{TmNi}_2\text{B}_2\text{C} \) below 13.5 K at zero field. The transition temperature increases and the accompanying deformation of the lattice is grossly enhanced when a field is applied along [100]. From the model analysis we conclude that this occurs mainly because the lattice is already close to the critical point due to the non-magnetic electron–phonon interaction. The magnetic interactions are the final ingredients that enforce the system to enter the quadrupolar phase, and the analysis indicates that the magnetoelastic crystal-field and the quadrupolar–quadrupolar interactions are of nearly equal importance, \( K(Q_A) = 0.46K_{\text{eff}}(Q_A) \). The quadrupolar ordering has the unique effect that a field applied along [100] induces antiferromagnetic ordering at the same wave vector as the quadrupolar ordering. The Fermi-surface nesting is presumably important for the strong electron–phonon interaction at \( Q_A \), and possibly also for the quadrupolar–quadrupolar interaction. Contrary to this, the RKKY interaction is concluded to be relatively weak at this wave vector. This suggests that those electrons, which are close to the nesting areas and important for creating the superconducting phase, are not the same as those determining the RKKY interaction. The present discovery has basic consequences for the understanding of the magnetism of the borocarbides.

It raises a number of questions: Is there a strain/charge quadrupolar phase in the non-magnetic borocarbides or a magnetic quadrupolar phase in other of the magnetic ones? Is the strong peak at \([0.55,0,0]\) in the exchange interaction of the Er compound, see Refs. \[13\] \[10\], a consequence of a quadrupolar interaction rather than the RKKY? Is the quadrupolar interaction the reason for the longitudinal polarization \[17\] of the antiferromagnetic ordered moments in the Tb compound? etc.

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