Magnetoelastic coupling in the organic radical β -*p*-NCC₆F₄CN₂SSN

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Resonant ultrasound spectroscopy (RUS) was used to analyze the elastic and anelastic behavior associated with canted antiferromagnetic ordering at 36 K in the radical, β -*p*-NCC₆F₄CN₂SSN, **1**. On cooling through the magnetic ordering transition there is anomalous elastic behavior away from the expected uniform stiffening with decreasing temperature, consistent with magnetoelastic coupling. The excess in the elastic stiffness follows the magnetic order parameter linearly below the magnetic ordering temperature. A much larger change in elastic properties is associated with short-range ordering between T_c and 150 K which appears to correlate with an excess heat capacity (and entropy). Thus it appears that the onset of long-range order to this spin canted system might only be a partial contribution to the whole phase transition.

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I. INTRODUCTION

The observation of a spontaneous magnetic moment in a purely organic (i.e. in the absence of a transition metal ion) material was first realized in 1991 with the discovery of ferromagnetism in the radical β -*p*-O₂NC₆H₄NIT (NIT = nitronyl nitroxide) at 0.65 K.¹ A number of radicals have been reported subsequently which also exhibit long-range magnetic order. Among these a number of thiazyl and selenazyl radicals have offered some of the highest reported magnetic ordering temperatures,^{2–9} of which the canted antiferromagnet β -*p*-NCC₆F₄CN₂SSN (**1**) is arguably the most well studied.^{10–17} Compound **1** was first synthesized by Banister *et al.*¹² who reported that it crystallizes in the orthorhombic space group *Fdd2* with unit cell dimensions $a = 15.105$, $b = 10.828$, $c = 11.933$ Å at 160 K. The structure of **1** is displayed in Fig. 1. Magnetic studies revealed that it is a canted antiferromagnet ordering at 36 K, with a canting angle of $(0.085 \pm 0.005)^\circ$. This spin canting leads to a small spontaneous moment which rises to $(1.5 \pm 0.1) \times 10^{-3} \mu_B$ as temperatures approach 0 K and hysteresis is evident at 1.8 K. The effect of pressure on the magnetic ordering temperature has been examined¹⁶ and it was found that increasing the pressure up to 16 kbar almost doubles the ordering temperature to 64.5 K. At ambient pressure there is a broad maximum in the magnetic susceptibility at 60 K, above the transition temperature, indicative of short-range antiferromagnetic ordering prior to undergoing long-range order to a canted antiferromagnetic state at 36 K.¹⁵ In addition, a clear excess in the heat capacity was reported, extending up to at least ~ 80 K^{10,17} implying that significant short-range ordering occurs above T_c prior to the onset of long range order at 36 K.

Neutron diffraction, antiferromagnetic resonance studies, muon spin relaxation, and dc SQUID magnetometry all reveal that the magnetic order parameter Q_m below T_c follows the Brillouin function^{11,13–15,17}

$$Q_m = Ng\mu_B S B_S(x), \quad (1)$$

where N is Avogadro's constant, g is the g factor which for **1** is 2.01,^{15,18} S is the spin, and $B_S(x)$ is the Brillouin function

given by

$$B_S(x) = \frac{2S+1}{2S} \coth\left(\frac{2S+1}{2S}x\right) - \frac{1}{2S} \coth\left(\frac{1}{2S}x\right), \quad (2)$$

where S is the spin angular momentum and x is given by

$$x = \frac{g\mu_B SH}{kT}. \quad (3)$$

Here H is the magnetic field and k is Boltzmann's constant. The magnetic order parameter varies between 0 in the paramagnetic/disordered state above T_c and 1 when fully ordered as T approaches 0 K.

Resonant ultrasound spectroscopy (RUS) has proved a useful tool in the analysis of phase transitions of minerals and metal bearing inorganic compounds.^{19–23} It provides a method of direct measurement of the elastic constants of a sample via measurement of its normal modes of vibration and therefore is sensitive to small changes in both molecular and solid state structure. Magnetic ordering transitions have been shown in some cases to be associated with changes in lattice constants,^{24–27} while in other cases there is no associated change in unit cell dimensions on cooling through the ordering temperature T_c .²⁸ If there is a change in crystallographic symmetry through the transition the behavior of the elastic constants can indicate the nature of the transition with respect to what order parameter is driving the transition and of the coupling between the order parameter and the symmetry breaking strain (distortion). If the strain which breaks the symmetry is the driving force for the transition (and therefore is the driving order parameter) then there would be linear elastic softening on either side of the transition (a true proper ferroelastic transition). For a magnetic transition, this mode of behavior would imply that the strain is the driving order parameter and thus that the magnetic order occurs as a result of this strain. If the symmetry breaking strain is not the driving order parameter for the transition but the transition is driven by some other process (such as magnetic ordering) then there are other possible modes of behavior depending on the relationship between the breaking of the symmetry and the order parameter for the transition. If the symmetry breaking

FIG. 1. (Color online) Structure of **1** viewed down the crystallographic b axis with unit cell displayed. Carbon atoms are displayed in gray, nitrogen in blue, sulfur in yellow, and fluorine in green. One of each atom is labeled in black. Short contacts between sulfur atoms in the heterocyclic ring and nitrogen atoms in the cyano group are labeled as dashed lines. A single unit cell is marked with c horizontal and a vertical.

strain and the driving order parameter are linearly coupled then the elastic constants should soften nonlinearly either side of the transition temperature (a pseudoproper ferroelastic transition). If the symmetry breaking strain couples with the square of the order parameter then a discontinuity in the elastic constants is expected with a jump in softening on cooling through T_c (an improper ferroelastic transition).²⁹ These patterns of softening are not always followed, however. For example, transitions involving hydrogen bonding in Lawsonite are accompanied by elastic stiffening²¹ and the ferroelastic transition in SrAl_2O_4 is also accompanied by stiffening.³⁰ In these two cases the stiffening can be treated in terms of an excess elastic constant with respect to the parent structure which scales with the square of the order parameter. Thus while RUS can provide a measure of the magnetic order parameter in the magnetically ordered phase, it can also provide valuable information on the behavior above the magnetic transition temperature where short-range interactions may be important. In this study we report elastic stiffening in β - p - $\text{NCC}_6\text{F}_4\text{CNSSN}$ which is clearly associated with the magnetic ordering and, in addition, we find stiffening between T_c and ~ 150 K which may be associated with short-range ordering. In addition, we have observed acoustic dissipation at frequencies of $\sim 10^5$ Hz which appears to indicate dynamic disordering above ~ 150 K.

II. EXPERIMENTAL METHODS

A sample of **1** was prepared according to literature methods¹² and characterized by microanalysis and solution EPR spectroscopy. Crystals large enough for RUS experiments were grown by slow sublimation under static vacuum (10^{-1} torr). The correct polymorphic (β) phase was confirmed by unit cell determination using x-ray diffraction. The single crystal sample used for RUS measurements was about 2 mm in all dimensions, with several well developed crystal faces, and weighed 0.0054 g.

A. RUS

The experimental RUS system consists of a single crystal sample held lightly between two piezoelectric transducers. The first transducer is driven by a frequency synthesizer at constant amplitude across a range of ultrasonic frequencies (0.1–2 MHz) which in turn causes the sample to resonate at

particular frequencies. The second transducer acts as a signal detector which records the response of the sample in terms of its displacement when it is vibrated across the frequency range. In the low-temperature head the sample is held lightly across a pair of faces or a pair of corners between the two transducers in a mount which is lowered vertically into a helium flow cryostat, as described by McKnight *et al.*²¹ Data were collected with the sample chamber filled with a few millibars of helium to allow heat exchange between the sample and the cryostat. The sample was cooled from 290 to 50 K in 30 K steps with a 20 min settle time, then from 50 to 10 K in 1 K steps with a 15 min settle time. The sample was then heated from 10 to 50 K in 1 K steps and from 50 to 290 K in 5 K steps, both sequences settling for 15 min at each temperature before data collection. For each spectrum 50 000 data were collected over a frequency range of 150–700 kHz.

All spectra were transferred to the software package Igor Pro (WaveMetrics) for analysis. Peak positions and widths at half height were determined for two peaks, at ~ 460 and ~ 510 kHz, by fitting with an asymmetric Lorentzian function. These two peaks were chosen because they were both present over the largest temperature interval. The mechanical quality factor Q was calculated using the relationship $Q = f/\Delta f$, where f is the peak frequency and Δf is the width of the peak at half its maximum height. The inverse of the quality factor Q^{-1} is a measure of acoustic dissipation (energy loss) within the sample.

III. RESULTS

To illustrate the general trend, RUS spectra collected in the interval 10–50 K are shown as a stack plot in Fig. 2. Temperature is scaled on the y axis with the high-temperature spectrum at the top of the stack and low-temperature spectrum at the bottom of the stack. Peaks in the spectra that are affected by temperature represent the vibrational frequencies of the normal modes of the sample and the square of the frequency of each mode is directly proportional to the elastic constants associated with that mode.³¹ Resonance modes of the crystal depend predominantly on shearing motions. Generally there is a uniform increase in peak frequency on decreasing temperature which is associated with normal thermal stiffening. Figure 3 shows the evolution of the square of the peak frequency and Q^{-1} for two peaks which have

FIG. 2. (Color online) Stack of RUS spectra for **1** between 12 and 52 K. The spectrum recorded at the magnetic ordering temperature 36 K is shown in blue and labeled on the right of the figure.

FIG. 3. (Color online) Evolution of the square of the frequency and the acoustic dissipation for two peaks at 513 (blue circles) and 463 kHz (red squares). Variations in f^2 are represented by open symbols and variations in Q^{-1} by closed symbols. Dashed line displays the magnetic ordering temperature 36 K. Solid curve is a baseline fit of Eq. (4) data above 150 K with θ_s set at 21 K.

frequencies 463 and 513 kHz, and which are representative of the behavior observed at other frequencies. It is clear that the data for f^2 deviate from linearity below ~ 150 K, with a further deviation at ~ 36 K before levelling off with further reducing temperature.

A. Elastic stiffening related to magnetic ordering below 36 K

In order to make a direct comparison of the elastic stiffening below 36 K with the degree of magnetic order, a baseline to represent the stiffness of the paramagnetic phase extrapolated into the stability field of the antiferromagnetic phase is required. This was obtained by fitting the function³²

$$f_{\text{baseline}}^2 = a_1 + a_2 \theta_s \coth \frac{\theta_s}{T} \quad (4)$$

to measured values of f^2 for the resonance peak near 450 kHz in the temperature interval 42–50 K, and is shown in Fig. 4. The saturation temperature θ_s produces the reduction in slope required by the third law of thermodynamics as T tends to 0 K. The difference between the observed f^2 values (magnetically ordered phase) and the baseline values (paramagnetic phase) Δf^2 was then scaled to vary between zero and 1, with the latter representing the excess stiffness at 10 K. This is shown as a function of reduced temperature T/T_c in Fig. 5. Spontaneous magnetization, antiferromagnetic resonance, and muon spin

FIG. 4. (Color online) Fit of Eq. (4) to the low temperature values of f^2 with $a_1 = 2.19 \times 10^{11}$, $a_2 = -3.56 \times 10^8$, and $\theta_s = 21$ K. Magnetic ordering temperature is represented by dashed line at 36 K.

FIG. 5. (Color online) Plot of the reduced excess of f^2 (proportional to excess elastic constant) calculated from the fit in Fig. 4 as a baseline (blue open circles), and the magnetic order parameter for $S = \frac{1}{2}$ (solid curve), along with corresponding experimental data for the order parameter determined from spontaneous magnetization (red crosses), antiferromagnetic resonance studies (open black squares), and muon spin relaxation experiments (solid purple circles). Within experimental error the variation of Δf^2 is indistinguishable from the variation of Q_m .

relaxation data have all been shown to scale linearly with the magnetic order parameter Q_m and are shown for comparison. The variation of Δf^2 is essentially indistinguishable from the other data, that is, the excess elastic constant scales linearly with the magnetic order parameter.

B. Elastic stiffening and short-range ordering below 150 K?

The RUS data in Fig. 3 reveal a clear deviation from normal elastic behavior below ~ 150 K. In order to test whether this might arise from short-range ordering ahead of the magnetic transition point, a different measure of an excess elastic constant has been compared with excess heat capacity. For this, the heat capacity data of Palacio *et al.*^{10,17} have been re-evaluated (Fig. 6). There is a small peak in C_p at 36 K, consistent with the onset of long-range order and Palacio *et al.* separated this contribution from the lattice contribution by subtracting a baseline fitted to data below 20 K and above 80 K. The underlying assumption was that 1 is fully ordered below 20 K and fully disordered above 80 K, with the baseline being adjusted until the result $\Delta S = 0.7R$ was obtained. This is the expected excess entropy for ordering of $S = \frac{1}{2}$ spins.

FIG. 6. (Color online) Original heat capacity data from Palacio *et al.*^{10,17} (black crosses) showing original baseline (blue, upper solid line) and new baseline (red, lower solid line).

FIG. 7. (Color online) Plot of the excess elastic constant squared (red crosses) and excess entropy (curve) below 150 K extracted from heat capacity data. Transition temperature is represented by solid vertical line for comparison.

To make a similar comparison with the elastic behavior over a wider temperature interval, a new baseline has been fitted to the data of Palacio *et al.* below 20 K and above 150 K with the polynomial

$$y = 1.01299 \times 10^{-6}x^3 - 7.41771 \times 10^{-4}x^2 + 2.42521 \times 10^{-1}x - 5.3 \times 10^{-1}. \quad (5)$$

This was subtracted from the observed C_p values to give an excess heat capacity ΔC_p and this in turn was integrated to give an excess entropy ΔS below 150 K based on

$$\Delta S = \int \frac{\Delta C_p}{T} dT. \quad (6)$$

An excess elastic constant Δf^2 for the same temperature interval was obtained by fitting a baseline with the form of Eq. (4) to the f^2 data above 150 K (Fig. 3) and then subtracting this from the measured values. In spite of these relatively crude treatments of the baselines, it can be seen that in the temperature range $10 < T < 150$ K the excess entropy, determined from heat capacity measurements, and $(\Delta f^2)^2$ have a remarkably similar evolution (Fig. 7). The exactness of the overlap may be fortuitous and the total excess entropy is clearly too large ($\sim \times 8$ of 0.7R) but there is at least some correlation between the two quite different properties.

IV. DISCUSSION

A. Elastic behavior in the magnetically ordered phase ($T < 36$ K)

At a phase transition there are almost invariably induced strains e which couple to the order parameter q . If the transition being investigated here is considered in terms of conventional strain/order parameter coupling, a starting point would be a Landau expansion with general form (without consideration of tensorial properties at this stage)

$$G(q, e) = G(q) + \lambda_1 eq + \lambda_2 eq^2 + \lambda_3 e^2 q + \lambda_4 e^2 q^2 + \frac{1}{2} C^\circ e^2, \quad (7)$$

where λ_n is the strain/order-parameter coupling constant. The excess free energy $G(q, e)$ thus combines terms in the magnetic order parameter $G(q)$ and the elastic energy $\frac{1}{2} C^\circ e^2$ as well as terms derived from magnetoelastic coupling, that is, terms in both e and q . $G(q)$ is usually written as a Taylor series expansion³³ but is not important in the present context since the form of elastic softening/stiffening depends to a large extent on the strain coupling terms. Symmetry rules determine which of these magnetoelastic coupling terms are allowed. The first term $\lambda_1 eq$ would cause a lowering of the symmetry of the orthorhombic structure (space group $Fdd2$) to monoclinic in the present case. The second term $\lambda_2 eq^2$ could give rise to a volume strain (normal magnetostriction) and, together, $\lambda_1 eq$ and $\lambda_2 eq^2$ would give rise to softening of the elastic constants at a displacive transition according to the equation of Slonczewski and Thomas³⁴ (see, for example, the review by Carpenter and Salje).²⁹ In the current case elastic stiffening is observed, indicating that this mechanism does not operate. Instead, the changes in elastic properties must be determined by the next coupling terms in e^2 . This leads to a change in elastic constants ($\Delta C = C - C^\circ$) according to

$$C = \frac{\partial^2 G}{\partial e^2} = C^\circ + 2\lambda_3 q + 2\lambda_4 q^2, \quad (8)$$

that is,

$$\Delta C = 2\lambda_3 q + 2\lambda_4 q^2. \quad (9)$$

Terms of the form $\lambda e^2 q^2$ are always permitted by symmetry so that, in the first instance, the relationship $\Delta C \propto q^2$ might be anticipated. The observation in this case that $\Delta C \propto q$ could indicate, however, that $\lambda_3 q e^2$ is the relevant term in the free energy expansion. Terms of this form are allowed for structural changes that do not involve a break in symmetry such as nonconvergent cation ordering.^{35,36} If q is symmetry breaking, such as is the case in magnetic ordering, terms of this form ($\lambda q e^2$) are only allowed for certain cases where q and e^2 transform as different irreducible representations (irreps) of the parent space group such that the product of the irreps contains the identity.

Use of the group theory program ISOTROPY³⁷ allows a more specific investigation of which coupling terms might possibly be responsible for the observed elastic stiffening. Starting with space group $Fdd2$, the active representation for magnetic ordering to give a canted antiferromagnetic ordered structure with magnetic space group $Fd'd2'$ ¹⁷ is $m\Gamma_3$. The magnetic order parameters for antiferromagnetic and canted antiferromagnetic ordering have the same symmetry and are expected to be linearly dependent; only a single magnetic order parameter Q_m is required therefore. In addition, a structural order parameter Q_s belonging to Γ_3 would give a symmetry reduction to a monoclinic structure with space group Cc , and the relevant strains are e_4 , e_5 , and e_6 . The latter transform as irreps Γ_3 , Γ_4 , and Γ_2 , respectively. The most obvious $\lambda e^2 q$ terms arise from combinations $\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$ and $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_3$ which each contain the identity representation. The first yields $\lambda e_5 e_6 Q_s$ and, hence, stiffening (for positive values of λ) as $\Delta C_{56} \propto q$. The second yields $\lambda e_1 e_4 Q_s$, $\lambda e_2 e_4 Q_s$, and $\lambda e_3 e_4 Q_s$ and, hence, possible stiffening in the same manner for C_{14} , C_{24} , and C_{34} . The situation for Q_m is quite different since magnetic order parameters change sign under time reversal,

and therefore terms involving odd powers of the magnetic order parameter cannot be invariant. This means that the equivalent terms with Q_m replacing Q_s are strictly zero and magnetic ordering alone cannot reduce the crystal system from orthorhombic to monoclinic. The reported structure at 12 K is orthorhombic,³⁸ in which case these elastic constants are all strictly zero. This leaves only the possibility that the structure is actually monoclinic, but with only very small distortions from orthorhombic lattice geometry and with strong (biquadratic) coupling between Q_m and Q_s . Symmetry breaking at 36 K would need to be driven, in part, by some slight change in crystal structure rather than by the magnetic ordering alone. In the absence of any evidence for such a transition, the alternative is that the slight stiffening may relate to the fact that the $Fd'd'2'$ structure is allowed by symmetry to be piezomagnetic. An externally imposed strain e_5 would give rise to a ferromagnetic moment aligned parallel to the z axis due to a term $\lambda e_5 Q_{\text{cantedAFM}} Q_{\text{FM}}$ and, since the induced magnetic order parameter (Q_{FM}) will be linear with e_5 , this could give a contribution to the shear modulus from C_{55} .

B. Elastic behavior in the region $T_c < T < 150$ K

In the interval 300 to 150 K the shear elastic constants represented by f^2 in Fig. 3 follow a normal (thermal) trend of stiffening with falling temperature. Below ~ 150 K, the trends become concave upward, suggesting that some additional contribution to stiffening occurs. At ~ 150 K there is a break in the trend of Q^{-1} , signifying that there is also a change in acoustic dissipation behavior at about this temperature. The pattern of Q^{-1} is similar to that seen above the structural phase transition in SrAl_2O_4 ³⁰ and seems to be characteristic of an order/disorder process. At high temperatures dynamic local disordering occurs at frequencies in the vicinity of an applied stress (~ 0.3 –1 MHz in this case) and there is sufficient coupling via the strain for dissipation (energy loss within the sample) to occur. At some temperature, in this case ~ 150 K, an ordered state becomes established, relaxation times for the local disordering process increase, the dissipation decreases and changes in elastic constants occur in proportion to the degree of order. In **1** this is consistent with the onset of short-range magnetic ordering prior to long-range order, as evidenced by the broad maximum in χ in the dc susceptibility¹⁵ and the contribution to the heat capacity above T_c .¹⁷

We have found an empirical relationship between the excess entropy ΔS and the combination of elastic constants C for a given acoustic resonance as $\Delta S \propto C^2$. The physical origin for the form of such a relationship is not clear but the most general implication is that some structural change ahead of the transition point gives rise to both entropy and elasticity changes. It appears that there is a degree of strain/order parameter coupling for some local order parameter which probably includes short-range magnetic ordering but must include structural contributions to account for the large value of ΔS . The correlation in Fig. 7 is speculative but, if valid, would indicate that the effects of long-range ordering below T_c contribute a lesser proportion of the total change in entropy and elastic stiffening with respect to the short-range order above T_c . In other words, the overall behavior involves the development of a high degree of short-range antiferromagnetic ordering followed by a very small change in the total order when this becomes long range at the actual symmetry breaking transition point.

V. CONCLUSION

Use of the RUS technique on a single crystal of β - p - $\text{NCC}_6\text{F}_4\text{CNSSN}$ has shown that the remarkable magnetic properties of this purely organic phase are accompanied by significant changes in elastic and anelastic properties. The pattern of anelastic losses is consistent with an overall order-disorder process. The patterns of elastic stiffening are consistent with a dominant influence on physical properties from the development of short-range order below ~ 150 K with a much smaller but quite distinct influence from magnetic ordering below 36 K. Linear scaling of the small elastic anomaly with the magnetic order parameter implies that the elastic stiffening associated with magnetic ordering is coincident with a lowering of the symmetry from orthorhombic to monoclinic or due to the onset of another phenomenon such as piezomagnetism.

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