NMR evidence for a metastable vortex arrangement in the two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

A. Van-Quynh
Laboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble I, 38402 Saint-Martin d'Hères Cedex, France

C. Berthier
Laboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble I, 38402 Saint-Martin d'Hères Cedex, France and Grenoble High Magnetic Field Laboratory, CNRS/Max-Planck-Institut für Festkörperforschung Grenoble, Boîte Postale 166, 38042 Grenoble Cedex 9, France

H. Mayaffre and P. Ségransan
Laboratoire de Spectrométrie Physique, Université Joseph Fourier Grenoble I, 38042 Saint-Martin d'Hères Cedex, France

P. Batail
Institut des Matériaux de Nantes, Université de Nantes, 44072 Nantes Cedex, France

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A metastable state of the vortex lattice in the two-dimensional (2D) organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ has been attested by ^{1}H NMR measurements. This metastable state, which could contain a substantial amount of vortex vacancies, is shown to be produced by the radiofrequency pulses used to detect the NMR signal. The creation of this metastable state is favored at the particular field $H_{\mathrm{max}}=0.8$ T, which is proposed as being the 3D-2D crossover field in this compound. From the temperature dependence of the anomalous line shapes generated by this metastable state, we deduce a temperature dependence of the in-plane magnetic penetration depth λ_{ab} between 0.14 and $0.4T_c$ consistent with an anisotropic superconducting gap, probably with lines of nodes. [S0163-1829(99)07217-3]

I. INTRODUCTION

Both high-T_c (HTSCs) and two-dimensional (2D) organic superconductors belong to the extreme type-II superconductor family. They display a rich magnetic field-temperature H-T phase diagram in the mixed state below the upper critical field H_{c2}. In conventional type-II superconductors an Abrikosov solid flux line lattice is expected in the field region between H_{c1} and H_{c2}.[1] Owing to enhanced thermal fluctuations, short coherence length and high anisotropy, the nature of the mixed state is considerably changed in the HTSCs and 2D-organic superconductors. It has been predicted[2,3] and observed[4] that the large thermal fluctuations result in the melting of the solid vortex lattice into a vortex liquid well below H_{c2}. Below a certain line in the H-T plane, called the irreversibility line, hysteresis is observable. This line separates a low field region, where the flux lines are pinned, from a high field one with unpinned vortices. The identification of this line with the melting curve was controversial until the observation of a first-order vortex lattice melting transition in $Bi_2Sr_2CaCu_2O_8$.[5,6] The layered structure and the high anisotropy of these new compounds leads to a model consisting of 2D pancake vortices, where the pancakes in neighboring planes interact via a combination of tunneling Josephson currents and electromagnetic interactions. Depending on the strength of these interactions the pancakes form vortex linelike objects with varying degrees of rigidity. The question of the effective dimensionality of the vortex lattice is a subject of intense interest. It has been predicted that above a 3D-2D decoupling line in the H-T plane the thermal fluctuations of vortex positions lead to a loss of coherence in the direction perpendicular to the conducting planes. In such materials vortex-lattice melting may occur in two separate stages: the melting of the lattice into a 3D liquid of vortex lines followed by loss of coherence between the layers.[7–9] The presence of defects and impurities in these new materials is responsible for the pinning of the flux lines, and in the solid phase, gives rise to a glassy state with diverging energy barriers instead of an Abrikosov vortex lattice.[10,11] Recent magnetization measurements in Bi- and Y-based compounds have revealed an unexpected second peak in the magnetization curves.[12,13] This second peak corresponds to an enhancement of the pinning and its significance is not yet clear. A model for a transition between a quasiordered ''Bragg glass'' and a disordered entangled vortex solid has been proposed.[14,15] The second peak has been also interpreted in terms of a dimensional crossover field B_{2D}.[16,17]

Here we give evidence for a metastable distorted state of the vortex lattice that is created by the application of radiofrequency pulses on a thin single crystal of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. These pulses, which are part of the NMR experiment, allow the direct observation of the metastable state, just after its creation. This state is characterized by a large anomalous diamagnetic screening which could correspond to the presence of vortex vacancies in the sample. In Sec. II we give an account of the experimental details and sample preparation. In Sec. III we recall the influence of a vortex lattice on the NMR line shape and describe how the unusual line shapes observed in our experiments have to be ascribed to a metastable distorted state of the vortex lattice. In Sec. IV we show that this state is indeed created by the rf pulses themselves, how it relaxes as a function of time, and how its appearance is maximized for a given value H_{max} of the external applied magnetic field. Furthermore, we show that the observed line shapes can be approximately reproduced by computer simulations of the field distribution due to a regular array of vacancies in a triangular vortex lattice. This allows us to interpret the temperature dependence of the NMR line shape, from which we are able to determine the temperature dependence of the in-plane penetration depth.

Finally, we discuss the field dependence of the phenomenon and propose to ascribe the maximum effect observed at H_{max} to the 3D-2D dimensional crossover field. This leads to a reasonable value of the anisotropy γ in this compound.

II. EXPERIMENT

We investigated the flux line lattice in a single crystal of the organic compound κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ by ^{1}H NMR. Single crystals were grown using a standard electrocrystallization process.[18] Two different platelike samples with typical size of a few mm$^2\times 40$ μm were studied. The crystal structure of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is monoclinic. However, in this paper we adopt the axis labels used for HTSCs, i.e., the c^* axis denotes the direction perpendicular to the ab conducting layers.

The measurements were performed in an electromagnet that allowed the applied field H_0 to be fully rotated in a plane containing c^* without moving the cryostat and the NMR probe. To avoid contamination by spurious proton signals and to maximize the filling factor, the NMR coil was wound directly around the sample sandwiched between two mica plates. The NMR signals were recorded using a modified CXP-125 Brücker spectrometer using a Nicolet LAS12/70 as a transient analyzer. The line shapes were obtained from the fast Fourier transform of half the spin-echo observed after the sequence $(\pi/2)_x-\tau-(\pi)_y$. The typical lengths of the $\pi/2$ pulses were short enough to irradiate the whole line (about 0.8–1 μs) and the acquisition dwell time was typically 0.25 μs. In most of the experiments the value of τ was set to 12 μs. The repetition time separating two spin-echo sequences is noted $D0$.

The temperature range of investigation was 1.5–4.2 K, the sample being immersed in liquid helium. As a consequence, its cooling rate down to 4.2 K was not fully controlled. We noticed that this could cause slight changes in the line shape at 4.2 K, which depends on the ordering of the ethyl groups in the crystal. In this context, slight structural phase transition around 80 K has indeed been recently reported by Aburto *et al.*[19] in the parent compound κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br. Such small changes, however, have no consequences on the results which are reported below.

III. THE MIXED STATE OF κ-(BEDT-TTF)$_2$Cu(NCS)$_2$

A. The *H*-*T* phase diagram

The κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ salt shows a superconducting transition around 10 K and has a layered structure which induces numerous anisotropic properties. This compound exhibits a similar crystal structure as that of HTSCs with alternating conducting and insulating layers (for details see Ref. 18). Moreover, due to the high value of the Ginzburg-Landau parameter ($\kappa\sim 60-100$) it belongs to the extreme type-II superconductors. Finally the short coherence length ($\xi_{ab}=5$–8 nm) and the high value of the Ginzburg number ($G_i\sim 10^{-2}$) similar to these of HTSCs permit to consider this compound as a model for the study of the mixed phase of the HTSCs. The relatively low value of the upper critical field [$H_{c2}(0)\sim 10$ T for the field applied perpendicular to the conducting planes and 20 T for the parallel field configuration] allows a complete investigation of the mixed state phase diagram. This vortex state has been studied in detail by transport measurements[20,21] and magnetization.[22] According to the phase diagram established in Ref. 23 our experimental device allows a detailed investigation of the low field and low temperature region of the *H*-*T* phase diagram ($1.50\leqslant T\leqslant 4.2$ K and $0.3\leqslant H\leqslant 1$ T), especially the solid vortex phase. Due to the low value of the critical current [$J_c(0)\sim 500$ A cm^{-2}] the vortex dynamic could be easily studied in superfluid helium with little risk of sample heating through the current leads and contacts. Bulaevskii *et al.*[24] have suggested a NMR study of the vortex dynamic in an anisotropic superconductor based on the study of the decay of the spin-echo amplitude and that of the spin-lattice relaxation rate in presence of a moving vortex lattice. Owing to the numerous advantages of the organic compound κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ exposed above, we have chosen it for such a NMR study.

B. Preliminary experiments

Before starting the NMR measurements with a moving vortex system we made preliminary spin-lattice relaxation rate measurements in order to confirm the peak of $1/T_1$ as a function of T, which was observed by several groups[25–27] and interpreted as the melting of the flux line lattice. We observed some surprising and unconventional NMR line shapes that we present below.

In Fig. 1(a) we plot the ^{1}H NMR spectrum obtained after field cooling at 0.35 T applied perpendicular to the ab conducting planes for two temperatures 1.50 and 4.2 K. At low temperature (1.50 K) the spectrum shows a low frequency (i.e., low field) tail that cannot be described by a triangular or square lattice of Abrikosov vortices.

Actually, in the field range $H_{c1}<H_0\ll H_{c2}$ (H_0 denote the external field) a square[1] or triangular[28] lattice of Abrikosov vortices does develop. It produces a periodic and inhomogeneous spatial field distribution $B(\vec{r})$ which causes the broadening of the NMR lines. $B(\vec{r})$ has the form[29]

$$B(\vec{r})=B_0\sum_{\vec{K}}\frac{\exp(-\xi^2K^2/2)}{1+\lambda^2K^2}\exp(-i\vec{K}\cdot\vec{r}),$$

where $\vec{K}$ are the vectors of the reciprocal lattice of the Abrikosov vortex lattice, B_0 the mean field induction, and λ and ξ the transverse penetration depth and coherence length, respectively. In the simple case where the vortices are parallel to the applied external field, this spatial variation of $B(\vec{r})$ leads to a frequency distribution for the NMR lineshape given by[30,31]

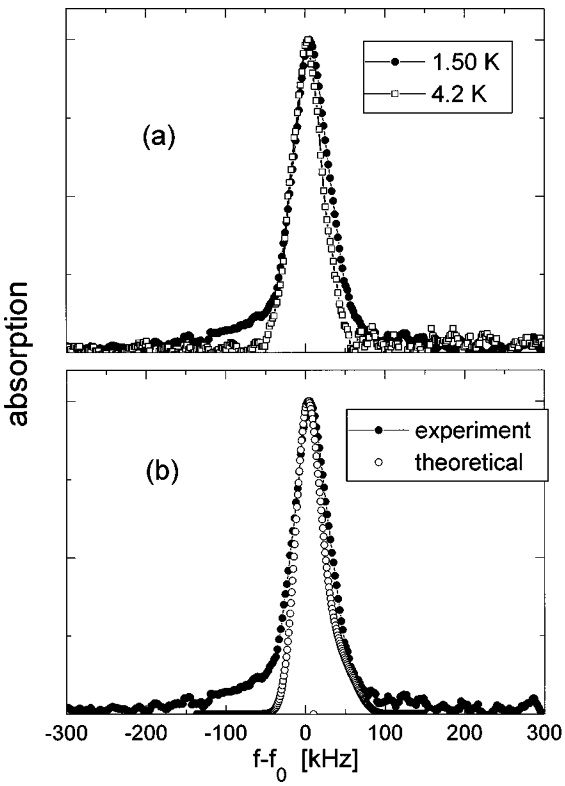

FIG. 1. (a) ^{1}H NMR spectra obtained after cooling in a field $H_0 = 0.35$ T perpendicular to the layers at 4.2 K (liquid vortex state) and 1.50 K (solid vortex state). Note the unconventional low frequency tail present at low temperature. (b) Comparison between the experimental spectrum obtained at 1.50 K and the theoretical line shape corresponding to a triangular vortex lattice with $\lambda_{ab} = 520$ nm and $\xi_{ab} = 8$ nm. Each spectrum is centered on the Larmor frequency.

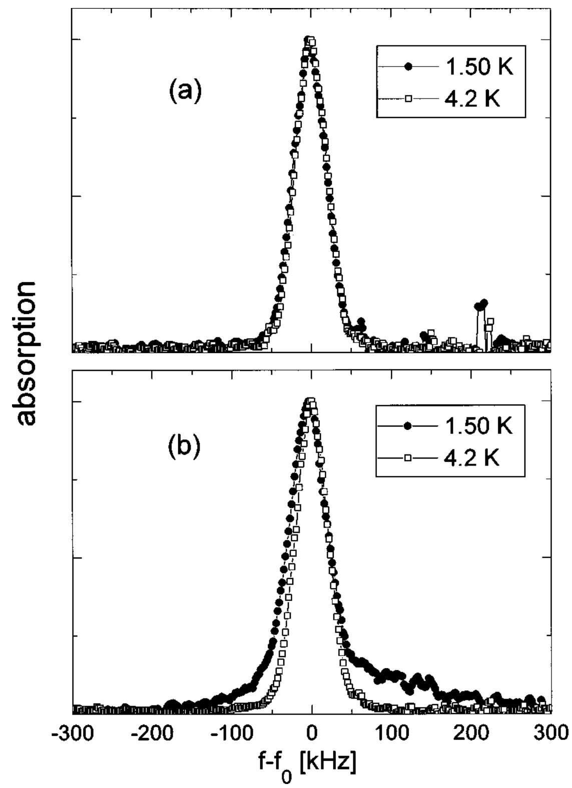

FIG. 2. (a) ^{1}H NMR line shapes for $H_0 = 0.35$ T parallel to the ab conducting planes after conventional field cooling. At low temperature no displacement or broadening are observed. (b) ^{1}H NMR line shapes after field cooling with $H_0 \| c^*$ down to 1.50 K and rotating the magnet so that H_0 is parallel to the conducting layers. The spectrum at 4.2 K was recorded after warming with H_0 parallel to the ab planes.

$$f(\omega) = \int \int \delta(\gamma_n B(\vec{r}) - \omega) \ d^2\vec{r}$$

in which $\vec{r}$ is a vector lying in a plane perpendicular to the vortex lines and γ_n is the gyromagnetic ratio of the observed nuclei.

The corresponding NMR line shape is asymmetric with two edge discontinuities and one singularity[30,32] and the second moment of the spatial field distribution $B(\vec{r})$ is related to the magnetic field penetration depth λ by

$$\langle \Delta B^2 \rangle^{1/2} = c \frac{\Phi_0}{\lambda^2}, \tag{1}$$

where Φ_0 is the flux quantum and c a constant depending on the vortex lattice geometry ($c = 0.06091$ for a triangular and 0.06219 for a square lattice[29]).

In the case of HTSCs and 2D-organic superconductors, which are strongly anisotropic, the topology of the vortex lattice and the corresponding field distribution depend on the orientation of the applied magnetic field,[33] but always lead to a large high frequency (i.e., field) tail in the NMR line shape. No structure at the low field side is expected, but the discontinuity due to the minimum of $B(\vec{r})$ which indeed is never observed.

To give more weight to our argument, in Fig. 1(b) we have superimposed on the experimental line shape a theoretical one obtained by computer simulation. This latter represents the expected field distribution for a triangular vortex lattice in a field of 0.35 T and for an in-plane magnetic penetration depth $\lambda_{ab} = 520$ nm and a coherence length $\xi_{ab} = 8$ nm. As we can see the low field broadening of the experimental line is inconsistent with a simple triangular lattice of vortices despite its high field part being in good agreement with the calculated one. To ensure that this anomalous line shape were really due to the presence of vortices we recorded, ^{1}H NMR line shapes for the external field parallel to the ab conducting planes following two cooling procedures.

(i) A field cooling with H_0 applied directly parallel to the ab planes. The corresponding spectrum is shown in Fig. 2(a) and no displacement or broadening of the line is observed at low temperature. According to Eq. (1) and to the fact that in this compound the transverse magnetic penetration depth λ_c is huge (> 30 μm), the presence of a vortex lattice should not be detected in a NMR spectrum. Moreover, if the single crystal is perfectly oriented in the external field, for $H_0 \| ab$ there are no normal vortex cores in the sample but only Josephson vortices between the conducting layers.

(ii) The sample was first cooled with the field parallel to c^* down to 1.50 K. After that the external field was rotated in order to bring H_0 parallel to the conducting planes. The corresponding experimental spectra are shown in Fig. 2(b).

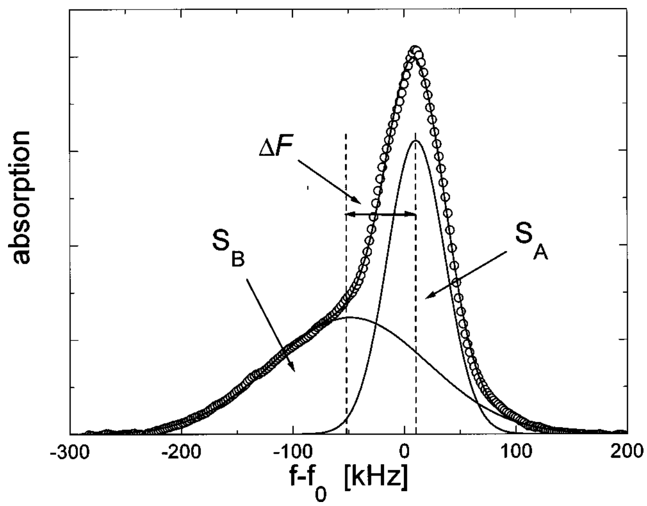

FIG. 3. Decomposition of an experimental spectrum into two Gaussians of area S_A and S_B, respectively. The separation between the centers of these Gaussians is denoted by ΔF.

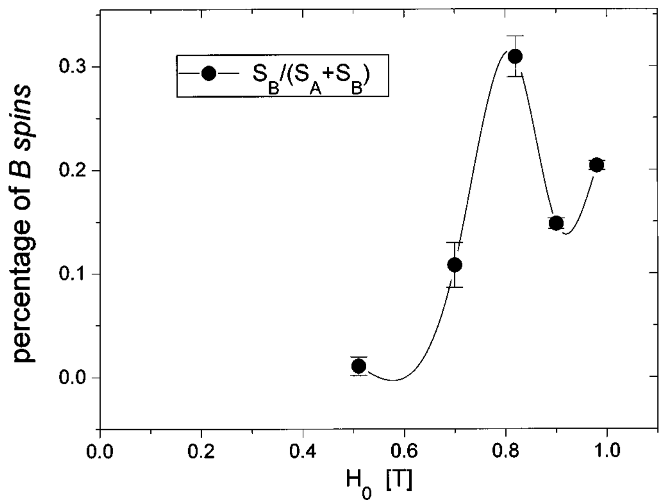

FIG. 4. Field dependence of the percentage of the *B spins*. Its behavior is unambiguously nonlinear but shows a maximum around 0.8 T. The line is a guide for the eye.

At the low temperature the same feature occurs as obtained with $H_0 \| c^*$. Then a necessary condition to observe the broadening of the line is to have created a vortex lattice with normal cores. This condition is satisfied when the sample is cooled with the procedure (ii). Even after the rotation of the magnet a vortex lattice should still exist, albeit deformed, pinned and probably unstable. The relaxation time toward the field-cooled situation at 1.50 K (i) is expected to be much longer than the delay before the NMR sequence was started.

When the sample is cooled with the field directly parallel to the planes, however, we do not observe the feature. In this case we have no normal vortex cores in the sample. This particular behavior was also observed at 0.5, 0.8, and 1 T.

IV. DEFORMATION OF THE VORTEX LATTICE

Such a surprising line shape, which has been observed only below 4 K, that is well below $T_c = 10.4$ K, could be the signature either of a new magnetic phase in the normal vortex cores or a deformation of the vortex lattice. In the first case, since the vortex cores density is proportional to the field magnitude (roughly $H_0 = n_V \Phi_0$), the amplitude of the low field tail should be also linear with the magnetic field. Then we recorded spectra at 1.50 K with the field parallel to c^* for several values of H_0 between 0.5 and 1 T. To estimate the part of the nuclear spins belonging to the low field line we fitted the spectra to the sum of two Gaussians (the area of the central one is denoted by S_A and S_B is the area of the low frequency one, see Fig. 3). The variation of the percentage of these nuclear spins [i.e., the ratio $S_B/(S_A+S_B)$] versus H_0 is shown in Fig. 4. Clearly this variation is not linear but shows a sharp maximum around $H_{\max} = 0.8$ T. This result allows us to rule out the hypothesis of a magnetic phase in the vortex cores and to retain that of a deformed vortex lattice.

We therefore have two sorts of nuclear spins in the sample, those that experience the normal magnetic field distribution (due to the presence of the Abrikosov vortex lattice), which we label as *A spins* and those that see a distorted field distribution (due to the deformation of the flux-line lattice), denoted by *B spins*.

A. Origin of the distorted vortex lattice

To characterize the spins that experience the deformation of the vortex lattice we studied the nuclear relaxation times of the two spin species. Although we did not measure the spin-spin relaxation time T_2 for the *B spins* precisely, the analysis of the spectra for various values of τ reveals that it is much shorter than for the *A spins*. This may explain why this type of line shapes has not been reported so far to our

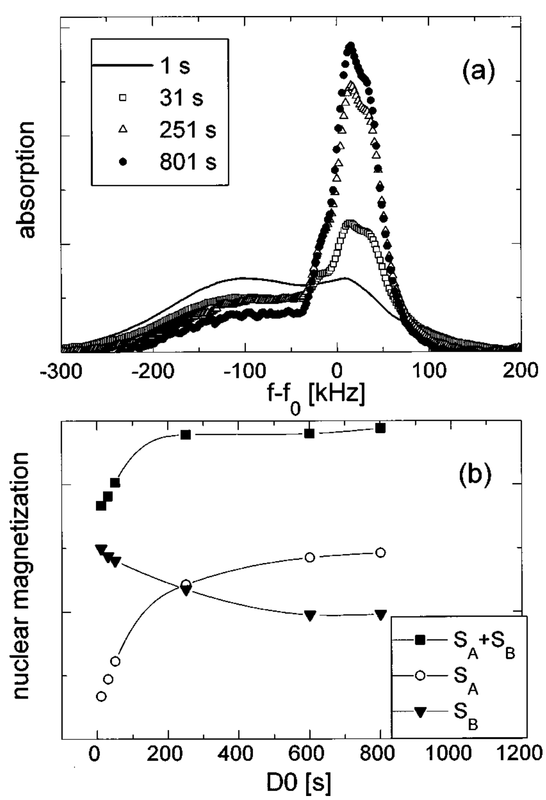

FIG. 5. (a) Dependence on the repetition time $D0$ of the ^{1}H NMR line shape at 1.50 K and 0.8 T. (b) Dependence of the nuclear magnetization of *A* and *B spins* (S_A and S_B) and of the total magnetization ($S_A + S_B$) as a function of $D0$.

knowledge. In Fig. 5(a) we report the variation with the repetition time $D0$ of the line shape for a fixed value of $\tau = 12\ \mu s$ and for a field 0.8 T applied parallel to c^* at $T = 1.50$ K. It appears clearly that the amplitude of the central line (*A spins*) increases with $D0$ while the amplitude of the low frequency line (*B spins*) decreases with $D0$. In two cases for long repetition times (>300 s) a constant amplitude is reached. To estimate the dependence on the repetition rate of the nuclear magnetization of the *A* and *B spins* we fitted the spectra to the sum of two Gaussians. S_A and S_B are the magnetizations M_A and M_B of the *A* and *B spins*, respectively. The magnetization M_i at time *t* could be expressed as a function of the number of nuclear spins N_i and the polarization p_i as follows:

$$M_i(t) = N_i(t) p_i(t).$$

The dependence of these quantities on $D0$ is shown in Fig. 5(b). The behavior of $S_B(D0)$ is quite unusual for a NMR experiment since the value of S_B is greater for short $D0$ than for long repetition times. Owing to the fact that the magnitude of transverse magnetization measured in a NMR spin-echo experiment cannot exceed its value at the thermal equilibrium such a behavior cannot be explained by any conventional NMR relaxation or cross-relaxation process. In addition, these effects are only observed for temperatures at which the vortex lattice is frozen, that is well below T_c. The only realistic explanation for the evolution of S_B is that the anomalous magnetic field distribution is created by the radiofrequency pulses themselves. For short $D0$ the deformation of the vortex lattice cannot heal and we are in presence of an cumulative process for which N_B, the number of *B spins*, increases rather than their polarization, p_B. That means that each echo sequence increases the number of nuclear spins that probe the deformation of the vortex lattice. Using Fig. 5(b) we can make a crude estimate of the characteristic relaxation time of the defects (about 150 s) and the value of S_B for long repetition times corresponds to the number of *B spins* seeing the distorted field distribution after a single spin-echo sequence.

At this stage we have established that the origin of these anomalous line shapes is due to a perturbation of the vortex lattice by the radiofrequency pulses. We now have to discuss the nature of this deformation, and by which mechanism it can be created. First, the low field part of the spectra reflects a strong local diamagnetic screening, indicating that part of the flux could be expelled from the crystal by the rf sequence. This can be quantified by comparing the first moment $\overline{B}_{1.5}$ of the distorted line obtained at 1.5 K with that of the undistorted one at 4.2 K, $\overline{B}_{4.2}$. We find $(\overline{B}_{1.5} - \overline{B}_{4.2})/\overline{B}_{4.2} \simeq 0.5 \times 10^{-3}$ which is indeed small. However, 20 to 30 % of the nuclei observed by NMR experience a strongly perturbed field distribution. This raises the problem of the penetration depth of the radiofrequency in the crystal and the fraction of nuclei that are detected in our NMR experiment. The penetration of an ac field in a superconductor has been discussed by many authors.[34–36] Different regimes are expected: in the liquid state or in the flux-flow regime, the penetration depth is quite large and corresponds to the skin depth associated with the Bardeen-Stephen resistivity.[34] In presence of a pinned vortex lattice generated by a static magnetic field perpendicular to the surface, and for an ac magnetic field directed along the surface, the radiofrequency penetration depth is $\lambda_{rf}^2 = \lambda_{ab}^2 + \lambda_C^2$ where λ_C is the Campbell penetration length, which is inversely proportional to the pinning strength. Experimentally, we find that the integrated intensity of the signal multiplied by the temperature to take into account the Curie behavior of the nuclear susceptibility, remains constant to within 20% in the temperature range 1.5–4.2 K, in spite of the fact that we cross the melting line. This indicates that the pinning is very weak, and therefore λ_{rf} is large. So due to the large amplitude of our rf field (typically 150 G, i.e., is four orders of magnitude larger than the ac magnetic field generally used to determine the temperature dependence of the magnetic field penetration depth[38]) we expect that all the vortex length will undergo subsequent tilt waves.[36] With the large value of the Ginzburg-Landau parameter κ, the flux line lattice of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ is expected to be soft (see for example Ref. 3) and that the flux lines can thus be bent easily. However, the mechanism by which the rf pulse sequence perturbs the vortex solid remains an open question, although we suspect that the platelike shape of the sample plays a role through the existence of a large surface barrier. Such an influence on the vortex solid has been recently studied in Bi-based compounds.[37] It appears that in the case of plate-shaped crystals the nonlinear transport properties do not reflect bulk vortex pinning properties and are determined predominantly by geometrical or surface barriers. Another point which should be clarified is the respective roles of the two rf pulses in the spin-echo sequence. The second pulse provides effective refocusing if the field distribution is the same before and after the π pulse. So considering that the Curie law for the nuclear susceptibility is satisfied in the temperature range 1.5–4.2 K, we observe all the nuclear spins and then we have to admit that only the first rf pulse is effective in the creation of the disordered vortex state and that at very short time (the μs scale) the efficiency of an rf pulse saturates very quickly.

B. What sort of defects?

The low field part of the spectra reflects a strong local diamagnetic screening. Our experiment cannot give a clear indication of how the *B spins* are distributed in the crystal. However, in order to quantify the effects observed in the line shape we have tried to model this strong local magnetic field anomaly by a distribution of vortex vacancies in the crystal. Recently Olive and Brandt[39] have calculated the interaction energy of vacancies and interstitials in a triangular vortex lattice for type-II superconductors in the London theory and shown that they are attractive. They found some metastable equilibrium configurations of the flux lattice around such point defects. We therefore calculated the magnetic field distribution for a triangular vortex lattice in which an 8×8 superlattice of vacancies is created. The field map for $H_0 = 0.8$ T is shown in Fig. 6 with the corresponding NMR line shape. We emphasize that we have chosen a very simple model for our calculations and although the calculated spectrum is not identical to the experimental one this computer simulation is rather consistent with our experimental measurements.

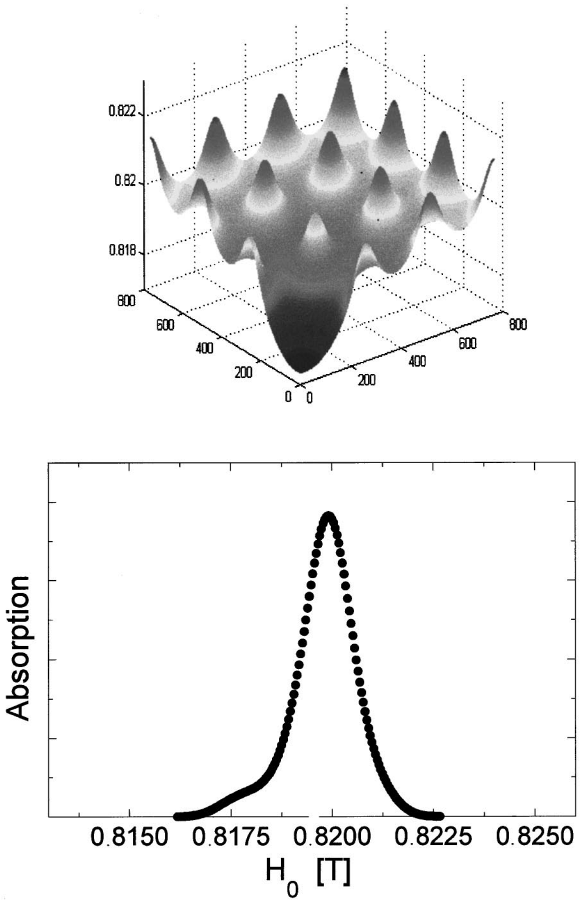

FIG. 6. Top: field map calculated for triangular vortex lattice (for an external field of 0.8 T with $\lambda_{ab}=520$ nm and $\xi_{ab}=8$ nm) in which an 8×8 superlattice of vacancies is created. Bottom: theoretical NMR line shape corresponding to the above field distribution. Note the presence of a low field tail, consistent with the experimental line shape.

C. Temperature dependence of the line shape

In Fig. 7 we show the temperature dependence between 1.50 and 4.2 K (i.e., $0.14T_c\leq T\leq 0.4T_c$) of the ^{1}H NMR spectrum at 0.8 T, where the magnetic field is applied parallel to c^*. Each spectrum is decomposed into two Gaussians. We denote by ΔF the separation (expressed in frequency) between the centers of these Gaussians. The temperature dependence of ΔF is shown for two values of the external field (0.8 and 0.98 T) in Fig. 8(a). It clearly appears that $\Delta F(T)$ is similar for each field value.

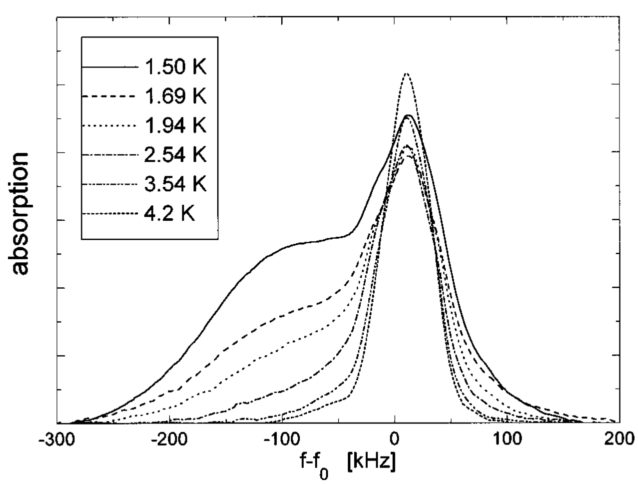

FIG. 7. Temperature dependence of the ^{1}H line shapes for a field of 0.8 T applied perpendicular to the conducting layers for $0.14T_c\leq T\leq 0.4T_c$.

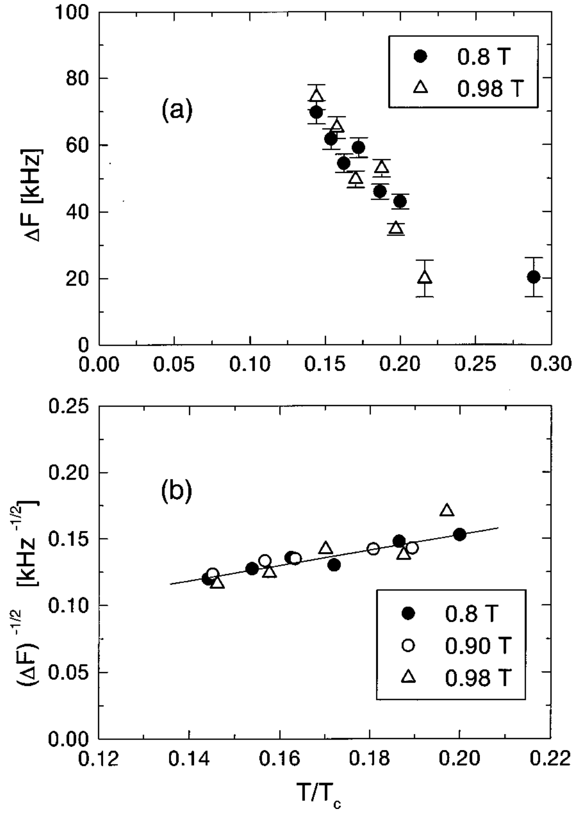

FIG. 8. (a) Temperature dependence of ΔF, the separation (in kHz) between the centers of the two Gaussians fitting the spectra of Fig. 7 for two values of the external field. (b) Temperature dependence of $\Delta F^{-1/2}$ for three values of the external magnetic field as a function of T/T_c ($T_c=10.4$ K). Note that $\Delta F^{-1/2}$ can only be reported for $T/T_c<0.3$ since the corresponding line shape is only observed for $T<3$ K. This variation reflects that of λ_{ab} with T and is consistent with an anisotropic superconducting gap with lines of nodes.

In the hypothesis of a lattice of vortex vacancies, the variation of ΔF with T can be related to that of the variation of the magnetic penetration depth λ. In the London theory the field distribution in presence of a regular lattice of vacancies can be calculated in the same manner as for a simple Abrikosov vortex lattice[29]

$$B(\vec{r})=B_0\left[\sum_{\vec{K}}\frac{\exp(-\xi^2K^2/2)}{1+\lambda^2K^2}\exp(-i\vec{K}\cdot\vec{r})\right.$$
$$\left.-\sum_{\vec{G}}\frac{\exp(-\xi^2G^2/2)}{1+\lambda^2G^2}\exp(-i\vec{G}\cdot\vec{r})\right],$$

where $\vec{K}$ are the vectors of the reciprocal lattice of the Abrikosov vortex lattice and $\vec{G}$ those for the vacancy lattice. Here the products $(\lambda K)^2$ and $(\lambda G)^2$ are much greater than 1 and the field distribution $B(\vec{r})$ is then proportional to $1/\lambda^2$. Since the NMR line shape corresponds to the histogram of $B(\vec{r})$, the separation ΔF will also scale with $1/\lambda^2$, as in the standard case [Eq. (1)], in spite of the peculiar form of the line shape.

From the temperature dependence of the line shape we can thus derive within this model the temperature variation of the in-plane magnetic penetration depth λ_{ab}. For this purpose we plot in Fig. 8(b) the variation of $\Delta F^{-1/2}$ with T for three values of H_0. All the points show the same variation as a function of temperature, independent of the magnetic field. Although a distinction between quadratic or linear behavior is difficult, there is a definite variation that cannot be explained by a conventional *s*-wave pairing. We have explored a temperature range below $0.4T_c$, and for a conventional BCS superconducting gap the magnetic penetration depth is expected to be constant for $T \leqslant 0.5T_c$. Our results are thus in favor of an anisotropic superconducting gap, possibly with lines of nodes, and they are consistent with the conclusion of several groups.[38,40]

V. FIELD DEPENDENCE OF THE PHENOMENON

In the introduction of Sec. IV we stated that the deformation of the vortex lattice was maximum around 0.8 T. Moreover we studied the temperature at which the deformation of the vortex lattice (i.e., the low field part of the line shape) starts to be reasonably observable on the spectrum. We fitted the spectra to the sum of two Gaussians (S_A and S_B denoting the areas). T_{max} corresponds to the temperature at which S_B/S_A+S_B is greater than 20%. It appears clearly that the effects of the radiofrequency pulses are maximum at 0.8 T at all temperatures. Considering the phase diagram in the *H-T* plane of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ we could attribute this field to the 3D-2D crossover. This value of 0.8 T is consistent with that where Friemel *et al.*[21] have observed a dramatic drop of the activation energies which was interpreted as a possible 3D-2D crossover. From the expression[9,41]

$$H_{\mathrm{cr}} = 2\pi \frac{\Phi_0}{\mu_0(\gamma d)^2} \ln\left(\frac{\gamma d}{\xi_{ab}}\right)$$

(where d denotes the interlayer distance, ξ_{ab} the transverse coherence length and γ the anisotropy, here $d = 1.52$ nm and $\xi_{ab} = 5-8$ nm) the value of the crossover field $H_{\mathrm{cr}} = 0.8$ T leads to an anisotropy between 145 and 160. This value is in agreement with the wide range of γ values found in the literature [from 20 (Refs. 42 and 43) to 350 (Ref. 44)].

The ''critical field'' deduced from our experiments seems, however, to be essentially temperature independent, which is not expected for the 3D-2D crossover field (see, for example, Ref. 45). Besides this dimensional crossover, another feature expected in the *H-T* phase diagram is a solid-solid transition from an ordered vortex crystal to a glassy state with enhanced pinning. The second peak observed in magnetization measurements in $Bi_2Sr_2CaCu_2O_8$ (Ref. 12) and in $YBa_2Cu_3O_{7-\delta}$ (Ref. 13) allows to separate a weakly disordered quasilattice (low field region) from a highly disordered entangled solid (higher field region).[15] This could also be an interpretation for our line shapes: at the transition the vortex solid could be in a critical state with a maximum ''sensitivity'' to the radiofrequency pulses. It should also be mentioned that at 0.8 T the temperature above which the phenomenon (i.e., the strong diamagnetic screening) disappears is about 3.5 K. According to the *H-T* phase diagram established by transport measurements in Ref. 23, the point (3.5 K, 0.8 T) belongs to the melting line. In this case the ''transition'' in the *H-T* plane corresponding to the maximum of vortex lattice deformation under radiofrequency pulses only exists below the melting line. This is reminiscent of the second peak in magnetization measurements observed in Bi-based systems.[12] A second peak in the magnetization curves has been also reported in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$.[17] However the anomaly in the magnetization curves appears at fields one order of magnitude lower that 0.8 T. The sample used for these measurements was ten times thicker than ours and here too it is possible that geometrical or surface effects occur. Finally, as it has been shown by Deligiannis *et al.*[13] and Khaykovich *et al.*[12] in HTSCs the position of the second peak strongly depends on doping, then on pinning and disorder.

VI. CONCLUSION

In conclusion, by anomalous NMR line shapes we have identified a metastable solid vortex state created by the radiofrequency pulses used in a NMR experiment. This state corresponds to a distorted flux line lattice and with a simple model of a periodic array of vortex vacancies in the crystal we manage approximately to reproduce our unconventional spectra. A detailed study of the line shapes with temperature allows us to derive a linear variation of the in-plane penetration depth with the temperature. Unconventional superconductivity seems thus to characterize κ-(BEDT-TTF)$_2$Cu(NCS)$_2$: our results are in favor of an anisotropic superconducting gap, possibly with lines of nodes. For the temperature range 1.50–4.2 K the effects of the radiofrequency pulses are strongest around 0.8 T. We attribute this field to the 3D-2D crossover field and derive a reasonable value of the anisotropy. Another explanation for this optimum field value could be found in the transition from a weakly disordered vortex solid to a glassy one in which the susceptibility of the vortices to the pulses could be maximum at the transition. Further measurements are necessary to characterize the deformation of the vortex solid and its evolution, such as local magnetization measurements, for example.

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