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Lattice gas ordering and associated charge density modulation observed by ^{77}Se NMR in the intercalated layered compound $\text{Li}_{0.5}\text{ZrSe}_2$ (*)

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Résumé. — La RMN du ^{77}Se démontre l'existence d'un ordre sur les lithiums dans $\text{Li}_{0.5}\text{ZrSe}_2$. En dessous de 250 K, la distribution des ions sur le réseau triangulaire est statique, et leur écran électronique entraîne une modulation spatiale du champ hyperfin du ^{77}Se . Seuls deux sites de sélénium sont observés. Le mouvement des ions entraîne une fluctuation du champ hyperfin responsable d'un pic de relaxation spin-spin vers 270 K.

Abstract. — We have observed lithium ions ordering in the intercalated layer compound $\text{Li}_{0.5}\text{ZrSe}_2$ through ^{77}Se NMR. Below 250 K, the lithium ions are frozen, and their screening charge causes a spatial modulation of the ^{77}Se nuclei hyperfine field. Due to lithium ordering, only two inequivalent selenium sites are observed. As the ions start moving, the hyperfine field modulation becomes time-dependent and its fluctuations cause a sharp peak in the ^{77}Se spin-spin relaxation around 270 K.

1. Introduction.

The interest in studying lattice gas ordering in intercalated transition metal dichalcogenides relies upon two peculiarities of these systems [1]. First, the mean occupation rate x of the vacant sites in the Van der Waals gap between adjacent sheets may be varied over a wide range. The lithium intercalated compounds are those offering the largest range of x variation without changing the host structure or stacking. Unfortunately no direct evidence of ion ordering has been obtained yet in these systems, in spite of speculations from electrochemical and thermopower [2] measurements. But order-disorder transitions have been demonstrated in $\text{Ag}_{0.33}\text{TiS}_2$ [3], Cu_xNbS_2 [4, 5] and some short-range order has been observed in Na_xTiS_2 [6]. The second interesting feature is that, in a naive rigid band model and supposing a complete ionization of the guest metal, fully intercalated compounds of the IVb group should become isoelectronic with the Vb group compounds, which are subject to periodic lattice distortions accompanied with charge density waves (PLD/CDW) [7]. Noting that the donor intercalation would rather increase 3-dimensional electronic properties, like in graphite compounds, one thus expects a

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competition between the two types of order, since the periodic potential due to the ordered ionic distribution has no reason to be commensurate with the CDW.

The Li_xZrSe_2 system is particularly suitable for studying these problems. First, Li_1ZrSe_2 is isoelectronic of 1T-TaS_2 , in which PLD/CDW are well known. Moreover, it undergoes a semiconductor metal transition on increasing lithium concentration at $x = 0.4$, as first observed by NMR [8], and confirmed by other techniques [9], including magnetic susceptibility [10]. It thus offers the ability of studying the influence of the electronic structure (metal or semiconductor) on the lithium ordering. In this letter, we shall focus on the concentration $x = 0.5$, which is in the metallic range and in which competition between lithium ordering and charge density wave instabilities is likely to occur. We show that lithium short-range order, and even lithium ion dynamics, can be reached through the observation of ^{77}Se nuclear magnetic resonance, which reflects the electronic screening of the guest ionic potential.

2. Experimental results.

The powder intercalated samples have been prepared by L. Trichet *et al.* by chemical intercalation using the n-butyllithium technique [11] from ZrSe_2 prepared as indicated in reference 10 with the stoichiometry $\text{ZrSe}_{1.91}$. Lineshape and spin relaxation measurements have been performed at 38.7 MHz and 57.3 MHz using a superconducting magnet and 1 KW Brücker transmitter. This frequency range has been chosen as a compromise between the gain in the sensitivity and the broadening of the line when raising the magnetic field. Using home-made saddled coil probes with nitrogen gas flow temperature regulation, we obtained rf rotating field of the order of 25 G with a total recovery time less than 8 μs . Due to their inhomogeneous width (20-50 G) the lineshapes were recorded by analogic Fourier transform of the echo (or half echo) using a boxcar integrator [12] and sweeping the magnetic field. The spin-lattice and spin-spin relaxation times have been measured using the usual π , $\pi/2$, and $\pi/2$, π pulse sequences, once their single exponential behaviour has been checked. The temperature dependence of the ^{77}Se lineshape

Fig. 1. — Temperature dependence of the ^{77}Se lineshape in the $\text{Li}_{0.51}\text{ZrSe}_2$ sample at 38.7 MHz. The arrows indicate the first moments of the lines referred to the ^{77}Se resonance in H_2SeO_4 .

in the range 170-290 K for the $x = 0.51$ sample is shown in figure 1. A single Lorentzian line is observed at room temperature, which is symmetric within the precision of experimental data. Its width is unexpectedly large (f.w.m.h. ~ 10 G at 38.7 MHz), field dependent, and exceeds the experimental resolution. It may partly be explained by the demagnetizing field associated to the Pauli susceptibility measured in this compound, $-\chi \simeq 13 \times 10^{-6} \text{ emu/cm}^3$ [10]. Below 250 K, it broadens and splits into a symmetric two-peak pattern, the splitting of which is proportional to the magnetic field, as checked by comparing measurements at 38.7 and 57.3 MHz. The temperature dependence of the spin-lattice, T_1^{-1} , and spin-spin, T_2^{-1} , relaxation rates of the ^{77}Se are reported in figure 2. Particularly striking is the sharp peak of T_2^{-1} which varies over two decades and exhibits a maximum at 270 K, which is the temperature at which the broadening of the line occurs. A small hump in the T_1^{-1} curve is also present in the same temperature region which is yet uninterpreted.

Fig. 2. — Temperature dependence of the spin-spin (T_2^{-1} : $\circ$, $\bullet$) and spin lattice (T_1^{-1} : Δ , $\blacktriangle$) relaxation rates of the ^{77}Se in the $\text{Li}_{0.51}\text{ZrSe}_2$ samples. Measurements were done at 38.7 MHz (open symbols : $\circ$, Δ) and 57.3 MHz (closed symbols : $\bullet$, $\blacktriangle$).

3. Interpretation and discussion.

As mentioned above, the splitting of the ^{77}Se lineshape observed below 250 K is proportional to the magnetic field. So it cannot be produced by the nuclear dipole-dipole magnetic interaction and must be due to the hyperfine magnetic coupling with the conduction electrons since the ^{77}Se has a 1/2 spin. Such a pattern cannot be the result of a powder distribution of non axial anisotropic magnetic shift, which in all cases exhibits but one infinite singularity, either a first possible explanation is thus the onset of an incommensurate PLD/CDW which is expected to give such a pattern due to the distribution of inequivalent ^{77}Se sites with different resonance shifts. Experimental lineshape and computer simulations of the patterns due to an incommensurate PLD/CDW of arbitrary single $\mathbf{q}$ wavevector are given in figure 3. The shape does not depend on the $\mathbf{q}$ wavevector, provided it is incommensurate, and that one neglects the presence of discommensurations; it departs from the shape observed in the case of triple PLD/CDW,

Fig. 3. — Experimental ^{77}Se lineshape in $\text{Li}_{0.51}\text{ZrSe}_2$ at 38.7 MHz and 188 K and computer simulations of the powder patterns due to an incommensurate charge density wave with $\Delta K^0 = 0.025\%$. The simulations include the finite width of the boxcar gated integrator and homogeneous Lorentzian broadenings with $\Delta H_L = 1.5$ kHz (---) and 4 kHz (...) in order to fit either the centre or the wings of the line.

more likely observed in the 2H-trigonally coordinated transition metal dichalcogenides [13]. We assumed that the ^{77}Se shift at site $\mathbf{R}_i$ is given by :

$$\Delta K(\mathbf{R}_i) = \Delta K^0 \cos(\mathbf{q} \cdot \mathbf{R}_i + \phi).$$

The fits include Lorentzian broadenings and take into account the finite width of the boxcar gate. Several trials adjusting ΔK^0 and the width of the Lorentzian were attempted, but none of them gives a really good agreement with experimental data. An improvement might be obtained with the introduction of anisotropic Knight shift, although such an anisotropy has not been observed at room temperature.

An alternative explanation is a modulation of the electronic charge density (at the Fermi level), at the Se sites, due to the screening of the lithium ions potential; such a screening will occur in the d-like conduction band, and will be reflected at the ^{77}Se nuclei through the p-d hybridization. The onset temperature of the transition will then correspond to the lithium ions freezing on the lattice gas, and the resonance lineshape will depend on the local order of these ions and the corresponding electronic screening. Two types of order can be expected for $x = 0.5$ on a triangular lattice gas [14], which both lead to two inequivalent Se sites in equal number. One of them, shown in figure 4, consists in an alternation of filled and empty parallel rows of lithium, and the corresponding screening can be viewed as a commensurate CDW with $\mathbf{q} = (0, 0.5)$, and $\phi = 0$ at the lithium sites. The corresponding fit is shown in figure 5 and is now in very good agreement with experimental data with $\Delta K^0 = 0.038\%$.

Fig. 4. — Projection along the c axis of the atomic positions in the ordered $\text{Li}_{0.5}\text{ZrSe}_2$ compound (a). Zirconium which also lies in a selenium octahedron (b) is not represented in (a). In the rectangular $a \times a\sqrt{3}$ lithium unit cell there are only two inequivalent selenium sites with either one or two first neighbouring lithium nuclei.

Fig. 5. — Experimental ^{77}Se lineshape in $\text{Li}_{0.51}\text{ZrSe}_2$ at 38.7 MHz and 188 K and computer simulation of the lineshape due to a commensurate charge density modulation with $\Delta K^0 = 0.038\%$ and $\Delta H_L = 5.5$ kHz. The wavevector ($q_1 = 0$, $q_2 = 0.5$) corresponds to the ordered state shown in figure 5 with the maximum amplitude at the Li positions.

In the case of random freezing of the lithium ions on the lattice gas, the expected pattern is rather difficult to calculate, since one deals with the screening of a concentrated random impurity potential. Taking into account only an additive first neighbour interaction gives a strong disagreement with experiment. Such a treatment is quite unrealistic, but we claim that a random lithium distribution, as soon as one considers a long-range electronic screening (Friedel oscillations), will not give such a well resolved two peaks pattern, but should lead to a broad symmetric line peaked at the average shift.

Therefore we consider the observed selenium NMR lineshape below 250 K as a clear evidence for at least short-range order of the lithium ions on their triangular lattice at $x = 0.5$. Above 270 K, the single ^{77}Se lineshape reflects an average hyperfine field corresponding to the mean occupation of the lithium sites.

If the last interpretation is correct, one expects the low temperature hyperfine field distribution to become time-dependent as soon as the lithium ions start moving, since the screening charge will readjust much faster than lithium distribution. Let us call $\delta h(\mathbf{R}_i, t) = \delta h^0 \phi(\mathbf{R}_i, t)$ the hyperfine field experienced by a peculiar selenium nucleus. Although the contributions of individual lithium ions to $\delta h(\mathbf{R}_i, t)$ are not simply additive, it is reasonable to consider that the correlation time of $\langle \delta h(\mathbf{R}_i, 0), \delta h(\mathbf{R}_i, \tau) \rangle$ is equal to τ_{at} , the average ionic hopping time. Thus the lineshape and the spin-spin relaxation time temperature dependence follows the usual features of the motional narrowing of the fine structure [15], that is T_2^{-1} proportional to τ_{at}^{-1} for $\tau_{\text{at}} \gg (\gamma \delta h^0)^{-1}$, maximum around $\gamma \delta h^0 \tau_{\text{at}} \sim 1$, and proportional to $(\gamma \delta h^0)^2 \tau_{\text{at}}$ at higher temperature. Experimentally, we deduce from the T_2^{-1} variation on the low temperature side of the peak an activation energy of 0.30 eV, very close to that measured from direct spin-lattice relaxation on the lithium itself [10], while the value of τ_{at} deduced from the resonance condition $\gamma \delta h^0 \tau_{\text{at}} \sim 1$ is in good agreement with that deduced from these data. We thus consider this T_2^{-1} behaviour as a definite proof that the ^{77}Se lineshape corresponds to the hyperfine field distribution resulting from the intralayer electronic screening of a frozen ionic distribution, which presents at least short-range order giving rise to two inequivalent Se sites ⁽¹⁾.

The onset of a PLD/CDW, through a divergence of the electronic susceptibility, could also provide a peak in the spin-spin relaxation through its dynamic fluctuations, but the temperature dependence would not be thermally activated and moreover, these dynamic fluctuations are usually pinned by charged impurities in those systems [13].

⁽¹⁾ Let us note that according to the ^{77}Se T_2 value at room temperature, a 4 gauss homogeneous broadening is included in the linewidth; at low temperature, the homogeneous broadening is negligible, but deviation from long-range order should induce a hyperfine field distribution which contributes to the linewidth.

In conclusion, we have observed, at a microscopic scale, the first evidence of inhomogeneous charge redistribution in the sheets of a host layer compound in order to screen the ionic potential of the ionized intercalant. This charge redistribution around lithium ions in intercalated transition metal dichalcogenides provides a contribution to the ion-ion interaction considered in the usual lattice gas Hamiltonian, which can be long-range. In the present case of $\text{Li}_{0.5}\text{ZrSe}_2$, the hyperfine field distribution gives evidence for short (or long)-range order giving rise to two inequivalent Se sites in equal number. X-ray and neutron diffraction studies are currently in progress to confirm this order-disorder transition. NMR work is also in progress in samples of lower and larger concentrations, in which various types of patterns have been observed. One expects the possibility of PLD/CDW formation only at large lithium concentration. A good insight on the lithium dynamic can also be provided by the ^{77}Se resonance. A similar effect could be applied to study the motion of spinless nuclei on a substrate containing low-abundant $1/2$ resonant nuclear spin, and also whenever an atomic order-disorder transition would affect the hyperfine field of neighbouring nuclei, like in $(\text{TMTSF})_2\text{ClO}_4$ [16] for example.

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