Confirmation of McMillan's Concept of "Discommensurations"

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^{77}Se NMR is used to study a proposal made by McMillan regarding the charge-density wave (CDW) in $2H$-$TaSe_2$. The dependence of the NMR line shape is compared with predictions based on McMillan's theory. McMillan's hypothesis of "discommensurations" is confirmed—that the so-called incommensurate CDW is best described by commensurate regions separated by regions of phase slip.

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The $2H$ polytype of $TaSe_2$ has anomalous properties which have been attributed to a *static* modulation in the conduction-electron density, a charge-density wave (CDW).[1,2] At high temperatures $2H$-$TaSe_2$ appears to be an ordinary metal, while at low temperatures a CDW is present with the hexagonal symmetry of its host lattice, but with the lattice constants perpendicular to the c axis *exactly* three times the lattice constants of the crystal.[1-4] The CDW is described by the sum of three plane waves with wave vectors perpendicular to the c axis and 120° apart. This low-temperature state is the so-called commensurate state. Above about 90 K the plane waves describing the CDW are found to change their wavelength by about 1% so that the CDW is no longer periodic with the lattice—the so-called incommensurate state. The CDW amplitude goes continuously to zero at about 120 K and the sample appears "normal" above 120 K.

Moncton, Axe, and DiSalvo[4] observed harmonics of the incommensurate CDW which they related to the third-order, or "lock-in", term in a free-energy expansion. To explain these results McMillan[5] has proposed that the spatial form of the incommensurate phase between 90 K and 120 K actually consists of commensurate regions separated by "phase-slip" regions which he called "discommensurations" so that the *average* wavelength is incommensurate. Nakanishi and Shiba[6] have extended McMillan's Landau model and show that the regions of phase slip can form a dislocation lattice in an otherwise commensurate CDW lattice. In this Letter we report the results of ^{77}Se ($I=\frac{1}{2}$) NMR measurements of line

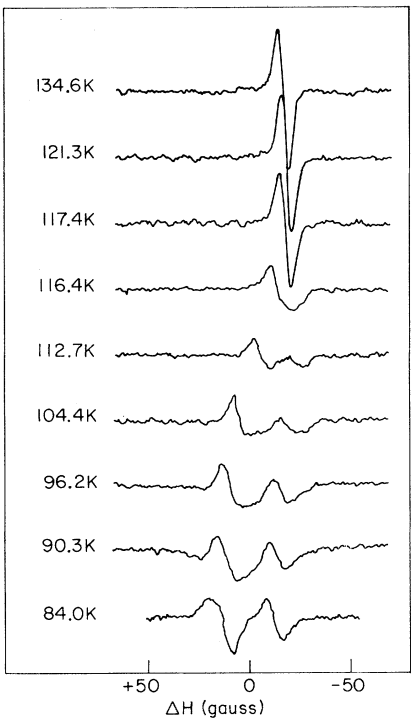

FIG. 1. NMR derivative spectra of ^{77}Se in $2H$-$TaSe_2$ as a function of temperature. Shown sequentially.

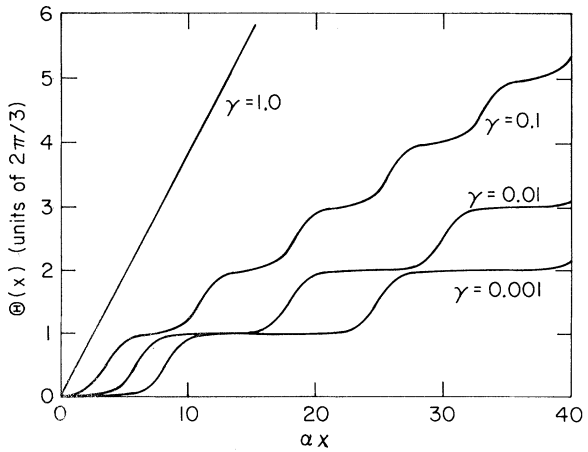

FIG. 2. $\Theta(x)$ as a function of αx for several values of the parameter γ showing the well-defined regions of "phase slip" which McMillan proposes for the CDW state in $2H$-$TaSe_2$.

shapes using a single-crystal sample of $2H$-$TaSe_2$ which confirm McMillan's proposal.

Previous NMR measurements on $2H$-$NbSe_2$ hint at the existence of discommensurations[7] but $NbSe_2$ has no commensurate CDW, and so a direct comparison between the incommensurate and commensurate CDW is impossible.

The concept of the NMR test is simple. In the commensurate state below 90 K, the unit cell of the CDW contains three distinct types of Se sites, each occupied by six Se atoms. Since the Knight shift of the NMR absorption lines depends on the charge density at or near the nuclear site, one should see three NMR lines of equal intensity. If McMillan is correct, a similar spectrum should also arise from the commensurate regions of the incommensurate state. On the other hand, if the incommensurate state were given by the picture which preceded McMillan's hypothesis, which we label the "conventional" incommensurate phase, the relative positions of the Se nuclei in the CDW unit cell would vary smoothly as one moved across the sample. The resulting NMR signal would be a smear instead of discrete lines. Moreover, as one went through the incommensurate-commensurate transition at 90 K there would be an abrupt change from a smear to discrete lines, rather than a gradual change as predicted by McMillan.

Since it has been reported that the transition temperatures for these materials are highly sample dependent,[8] we performed precision electrical resistance measurements to locate the transition temperature for our NMR sample. The details of these measurements will appear in a separate paper. We found transitions at 90 K on heating and cooling and a transition at 110 K which occurred only on heating, in agreement with the recent x-ray diffraction study of Fleming,[9] *et al.*, showing that the CDW in our sample is in an incommensurate state between 90 K and 120 K.

Figure 1 shows several of our NMR absorption derivative spectra. They are all taken at 42 MHz with the field parallel to the c axis. Qualitatively one immediately sees that the changes in the spectra appear to be continuous from a single line in the normal phase to three lines with roughly equal areas in the commensurate phase. To be more quantitative we have developed the following formalism to simulate line shapes with a CDW present.

Quite generally we can express the spatial variations of the charge density as a commensurate wave distorted by a modulating function. The Knight shift must have the same spatial periodicity. We write the Knight shift for a nucleus

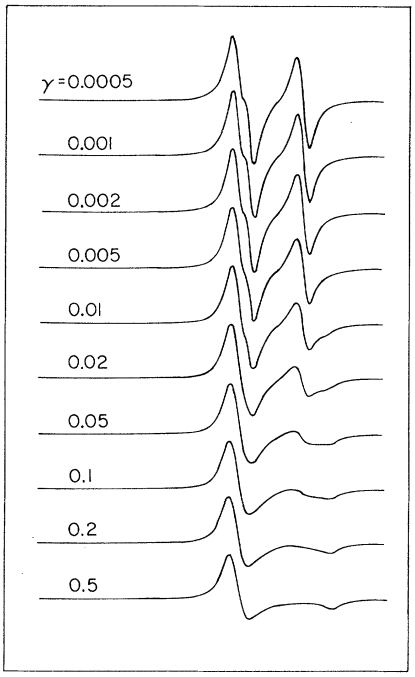

FIG. 3. Theoretical NMR spectra in the presence of a charge-density wave for various values of γ.

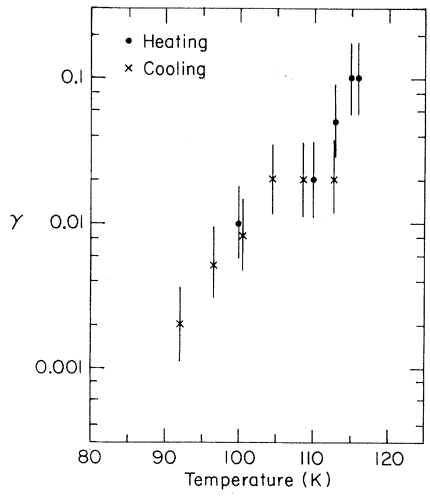

FIG. 4. The parameter γ obtained from a least-squares fit to the NMR data. The error bars give an indication of the statistical error of the fit.

at a position $\vec{r}_i$ as

$$K(\vec{r}_i) = K_0(T) + K_1(T)\sum_j \cos[\vec{q}_j \cdot \vec{r}_i + \Theta_j(\vec{r}_i) - \Theta_{j+1}(\vec{r}_i) + \Theta_0], \quad (1)$$

where K_0 contains all terms which are common to all nuclei and may depend on temperature, K_1 is related to the amplitude of the CDW which we will take to be independent of $\vec{r}_i$, Θ_0 is the common phase angle of the three plane waves at $\vec{r}=0$ (a Ta site), and the $\vec{q}_j$ have the same magnitude and point in the same direction as the wave vectors of the commensurate CDW. The phase angles $\Theta_i(\vec{r})$ will effectively translate the origin as a function of $\vec{r}$ and we have defined $\Theta_4(\vec{r}) = \Theta_1(\vec{r})$.

The contribution to the total NMR signal, $S(\omega)$, from the nucleus at $\vec{r}_i$ is written as a line-shape function, $g(\omega;\vec{r}_i)$, centered at the frequency given by Eq. (1). We take $g(\omega;\vec{r}_i)$ to be Lorentzian. We do the sum over all sites by integrating over the Θ_j's with a weighting function, $\eta(\Theta_j)\,d\Theta_j$, corresponding to how often a particular phase angle occurs.

To calculate $\eta(\Theta)$ we take the equation for $\Theta(x)$ which McMillan derives assuming only phase modulation is important and integrate once to obtain

$$\eta(\Theta) \propto \alpha(dx/d\Theta) = [\sin^2(3\Theta/2) + \gamma^2]^{-1/2}, \quad (2)$$

where α is defined by McMillan, and γ^2 is an integration constant.

The limiting cases are then (i) commensurate ($\gamma \to 0$), $\eta(\Theta) = \delta(\Theta)$, and (ii) conventional incommensurate ($\gamma \to \infty$), $\eta(\Theta) =$ constant. For McMillan's picture we have a situation between (i) and (ii). We show Θ as a function of αx for several values of γ in Fig. 2.

For the normalized signal generated by Eqs. (1) and (2) we apply the formalism of Wind and Emid[10] in reverse to generate "experimental" derivative spectra. In Fig. 3 we show theoretical NMR spectra for various value of γ, demonstrating the strong dependence of the line shape on γ. We emphasize that the size of γ alone determines whether one has a commensurate, conventional incommensurate, or McMillan incommensurate line shape.

We have fitted our data with this simple model to determine the values of γ and K_1 as a function of temperature (Figs. 4 and 5). We found that the intensity of the NMR spectra were roughly independent of temperature and we could take $\Theta_0 = 0$ for all spectra in the incommensurate region though there are several values which would give similar results. The half-width at half maximum of $g(\omega;\vec{r}_i)$ was found to be roughly constant around 4 G. It is clear that between 90 and 120 K the spectrum is described by values of γ which correspond to McMillan's concept of a CDW with well-defined regions of phase slip.

In Fig. 6 we demonstrate how well our model

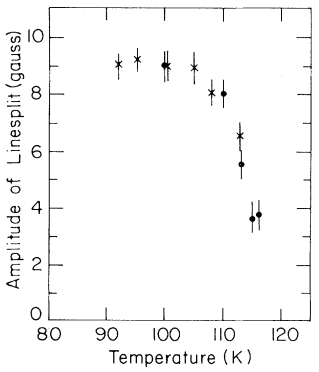

FIG. 5. The amplitude of the NMR splitting, K_1, obtained from a least-squares fit to the NMR data.

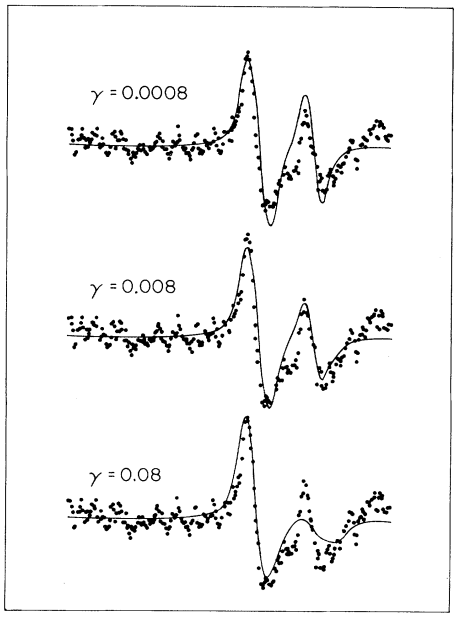

FIG. 6. A comparison of the "best fit" theoretical curve, $\gamma = 0.008$, and a theoretical curve which is more commensuratelike, $\gamma = 0.0008$, and one which is more incommensuratelike, $\gamma = 0.08$, for an NMR spectrum taken at 100 K on the cooling cycle.

can simulate a spectrum in the "incommensurate" region and show the substantial deterioration of the fit when we take γ to be either ten times or one-tenth the γ which gives the best fit. It is clear that the spectrum at 100 K gives a value of γ which we see from Fig. 2 exhibits a definite commensurate component. Thus we confirm McMillan's picture of the incommensurate phase.

Nakanishi and Shiba found that one should also include amplitude modulation. Moreover, it is possible that the width of $g(\omega;\vec{r}_i)$ is modulated. Such effects may account for the residual discrepancies between our line-shape theory and data. However, for the values of γ we obtain, the line shapes are insensitive to amplitude modulation (proportional to the phase modulation) of up to 50%.

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Direct Measurement of the Bulk Density of Gap States in *n*-Type Hydrogenated Amorphous Silicon

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The first direct measurement is reported of the bulk density of deep states in *n*-type *a*-Si:H. The spectral distribution is considerably different from previous field-effect and *C-V* measurements and the overall density is much lower than has previously been reported. The states seen in these samples appear to be extrinsic and suggest that the extrapolated total density of deep states in pure *a*-Si:H may be less than 10^{15} cm^{-3}.

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Recently, there has been considerable interest in determining the concentration and energy distribution of states in the gap of hydrogenated amorphous silicon. This stems from the fact that nearly all of the important transport and optical properties of this material are influenced by these gap states. The most widely accepted techniques for obtaining such information have been field effect[1] and metal-oxide-semiconductor *C-V* measurements.[2] However, these methods are rather indirect and may be influenced by states located near the surface. In this Letter we report the first measurement of the spectral distribution of gap states in the bulk of *n*-type *a*-Si:H. Our results differ quite markedly from those of previous measurements.[1,2]

The techniques which we employ are well known in crystalline semiconductors and are generally referred to as space-charge spectroscopy.[3] Such techniques have recently been applied to *a*-Si:H,[4,5] but these early results were not definitive enough to yield a complete picture of the density of gap states. Since these methods as well as field-effect and *C-V* measurements are based on space-charge layers, it is essential to understand the differences between these techniques. In field-effect and *C-V* measurements one changes the bias voltage which simultaneously varies *both* the width of the space-charge layer and the intersection of the Fermi level with the density of states. The data are thus a convolution of the energy *and* spatial variation in gap states. All anal-