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Effect of radiation damage on the charge-density-wave dynamics in $NbSe_3$

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We have used 2.5-MeV protons to produce radiation damage in $NbSe_3$, in a homogeneous controlled manner. The defect concentration was varied from 10 to 500 ppm in order to study the effects of pinning on the charge-density-wave motion. Measurements were made of the nonlinear conductivity, the threshold electric field, and the dielectric constant and conductivity as a function of frequency in the range 0–100 MHz. We find that the threshold field and the reciprocal dielectric constant vary linearly with the defect concentration and hence the restoring force.

$NbSe_3$ is an anisotropic metal which exhibits two large resistivity anomalies at $T_1 = 145$ K and $T_2 = 59$ K.[1] Transport[2,3] and x-ray[4] measurement have shown that these are incommensurate charge-density-wave (CDW) transitions. Perhaps most interesting is the observation of a strongly frequency- and electric-field-dependent conductivity in the region below each of these transition temperatures.[2,3,5-8] Several authors have attributed the non-Ohmic behavior to a depinning of the CDW by the eletric field.[3-10]

An essential ingredient to all models and theories of the non-Ohmicity is the pinning of the charge-density wave by impurities or imperfections.[9,10,6] In order to investigate the properties of $NbSe_3$ crystals as a function of the pinning force or density of pinning sites, we have performed radiation-damage experiments using 2.5-MeV protons. Experimental details of the irradiation will be published elsewhere.[11] For the proton energies and sample thicknesses used, the defect concentration was uniformly distributed throughout the sample and easily controlled by the current and exposure time.

Ong *et al.* have reported the effect of substitutional impurities in $NbSe_3$ on the characteristic field for non-Ohmicity.[6] At the time of their first work the functional form of the nonlinearity was not well established. More recent experiments have shown an actual threshold electric field above which the non-Ohmic behavior is observed.[5] The present work was undertaken in light of the new findings and the difference between substitutional impurities and defects to compliment the previous work. Brill *et al.*[6] have also recently completed a study of impurity effects taking into account the threshold fields.

Detailed electrical conductivity measurements from 300 to 4 K were performed for all of the samples reported here and to much higher defect concentrations. Extensive studies will be published elsewhere. For concentrations up to 500 ppm the fractional increase in the resistivity of the samples at the CDW transitions was essentially unchanged from that found in nominally pure samples. The transition temperatures shifted to slightly lower values ($T_1 = 141$ K, $T_2 = 56$ K for 500 ppm) but the CDW transitions were obviously still present. At 4.2 K the resistivity plotted as a function of radiation dosage was linear up to 500 ppm, indicating that the number of displaced atoms is proportional to the dose. The linear relationship between resistivity and damage allows us to use the resistivity ratio $[R(300\text{ K})/R(4.2\text{ K})]$ as a relative measure of defect density. The absolute value of the defect density can only be calculated to a factor of 2 while the relative value is accurately known.

The non-Ohmic conductivity was obtained from both pulsed and dynamic resistance measurements. The pulsed technique was used to avoid sample heating in the more highly damaged samples. Pulse widths were typically 1–10 μsec with repetition rates of 0.001–1 kHz. Leads were either made of gold wire which was silver-painted to the sample, or else indium solder was applied directly to the $NbSe_3$. The better contacts were those which were indium soldered. The four-probe technique was used for low-frequency conductivity measurements and two-probe for the frequency dependence.

The electric-field dependence of the resistivity is shown in Fig. 1 for a pure sample and for a sample after irradiation. The different temperatures used correspond approximately to the temperature at which the respective resistivities are maxima. In both cases there is a relatively well-defined threshold field above which the resistivity quickly falls and tends to saturate. The total change in resistivity is seen to be substantially

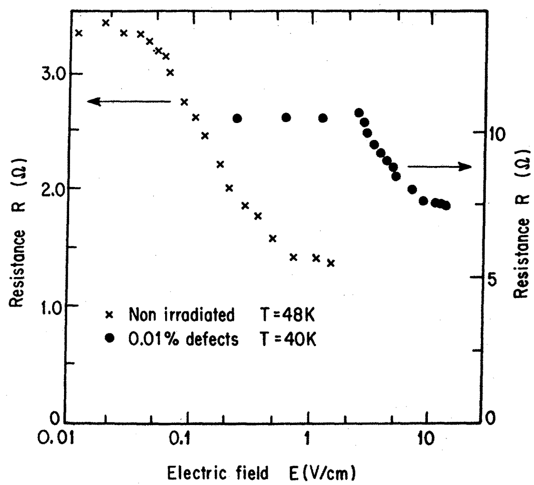

FIG. 1. Chordal resistance of $NbSe_3$ as a function of electric field for a pure and a radiation-damaged sample. Temperatures correspond to the minimum threshold field in the two cases.

less for the damaged sample.

In Fig. 2 we have shown the temperature dependence of the resistance of a sample of $NbSe_3$ which had been damaged with ~0.01% defects. The data were taken for several electric field strengths. The CDW transition at 59 K is clearly observed and shows negligible temperature shift. The resistance increase below the transition is less sharp than observed in undamaged samples. The large differences are the scale of the electric field (volts per cm rather than tens of millivolts per cm and the value of the low-temperature (4.2 K) resistivity, which is more than an order of magnitude higher than what one finds for typical undamaged samples. Of particular interest is the saturation value of high-field resistance obtained by fitting our data to the functional form given by Fleming and Grimes.[5] In pure $NbSe_3$ the saturation value coincides with the resistivity value extrapolated from above the CDW transition. In the present work the saturation value is considerably higher than the extrapolated value. If the additional conductivity is to be associated with the motion of depinned CDW's, it should be noted that the CDW limiting conductivity (and not merely the threshold field) is affected by impurities.

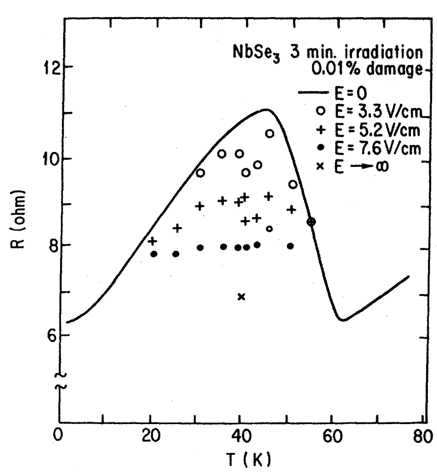

FIG. 2. Temperature dependence of the resistance of an irradiated sample for several field values. Note the extrapolated high-field saturation value.

The temperature dependence of the threshold field (E_T) for several defect concentrations is shown in Fig. 3. As a function of temperature E_T has a minimum at the temperature where the peak in the resistance occurs. As the radiation damage is increased this minimum becomes less pronounced, and appears to shift to a lower temperature. This is consistent with the resistivity measurements where a decrease in T_{CDW} was observed in the irradiated samples as well as a smearing of the transition. An increse in E_T is seen as one progresses to higher doses of radiation.

In order to investigate the variation of E_T with

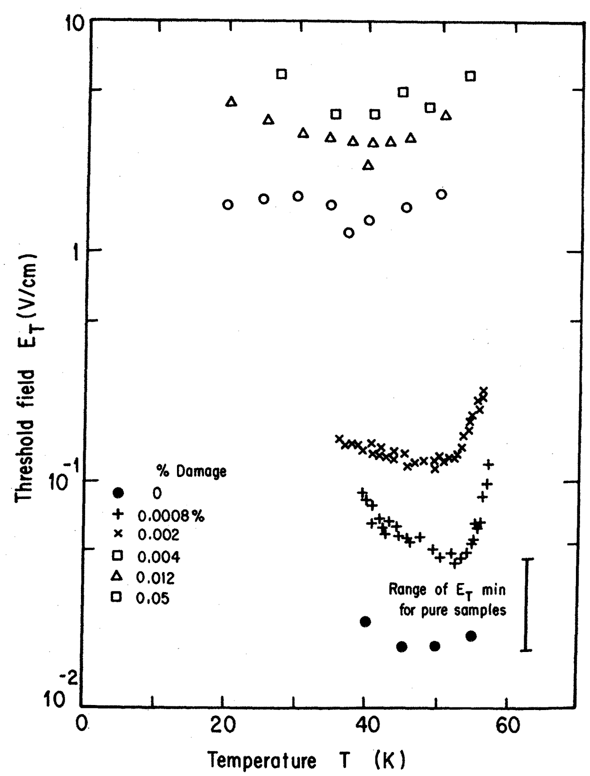

FIG. 3. Threshold electric field as a function of temperature for several dosages of irradiation.

the number of irradiation-induced defects, E_T is plotted against one over the residual resistance ratio in Fig. 4. The number of defects is well measured by the residual resistance ratio as the estimated damage scales linearly with the reciprocal resistance ratio. In Fig. 4 we see that E_T increases linearly with the inverse of the residual resistance ratio. Thus E_T scales linearly with the number of defects in the material. Lee and Rice[9] predict a linear dependence of E_T on defects if the defects are strong CDW pinning centers. The radiation-induced defects can be interpreted, therefore, as causing strong pinning of the CDW.

These results may be compared with the earlier work of Ong *et al.*[6] who studied the effects of substitutional impurities of the non-Ohmic behavior. They interpreted their results in terms of a characteristic electric field E_0 which is not directly related to the threshold field E_T used in more recent work. They found that E_0 varied quadratically with the residual resistivity; more recent work also shows that E_T varies quadratically. An explanation in terms of the theory of Lee and Rice would suggest that the substitutional impurities acted as weak pinning sites while the defects are strong pinning sites. While at face value this seems reasonable it should also be noted that studies of thermoelectric power and superconductivity indicate that even isoelectronic impurities of sufficient density destroy the charge-density waves.[12] By contrast even heavily damaged samples, with much larger residual resistivities, always exhibit CDW transitions.[11]

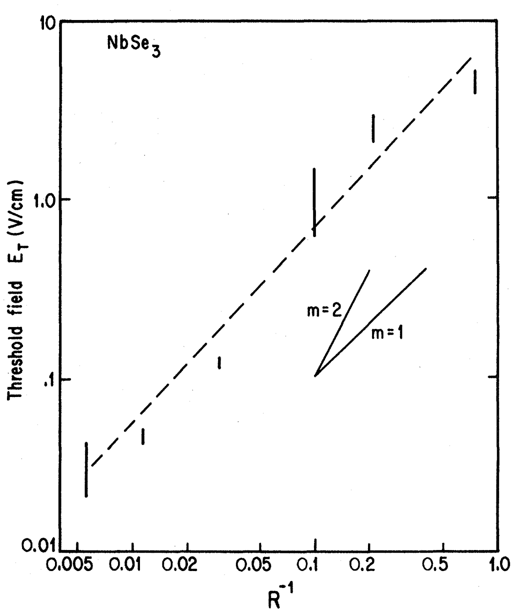

FIG. 4. Threshold field as a function of inverse resistivity ratio R(4.2 K)/ R(300 K) showing the linear relation.

The frequency dependence of the conductivity was measured using the bridge method, of Grüner *et al.*[8] The samples were mounted using a two-probe technique. The sample impedance may be represented by an *RC* circuit. By balancing the resistive part of the circuit with a variable resistor, the real part of the conductivity can be determined since $\mathrm{Re}\sigma(\omega) = 1/R$. The imaginary part of the conductivity is found from balancing the capacitive part of the circuit with a variable capacitor $\mathrm{Im}\sigma(\omega) = \omega C$. It was possible to calibrate the out-of-phase component using the relation $\mathrm{Im}\sigma(\omega)/\mathrm{Re}\sigma(\omega) = RC\omega$.

The temperature dependence of $R(\omega)$ is shown in Fig. 5. It can be seen that the resistance has a frequency dependence ($\omega < 100$ MHz) only in the temperature range where the CDW anomalies appear. The lower-temperature CDW shows a stronger frequency dependence in this frequency range than the upper transition.

The temperature dependence of the dielectric constant for several frequencies is shown in Fig. 6. For frequencies above 10 MHz the capacitance decreases with increasing frequency for the defect concentration shown. Here too it is the lower transition that exhibits the higher reactance. This is in agreement with what Grüner *et al.*[8] found for the nonirradiated $NbSe_3$.

The conductivity change with frequency is plotted in Fig. 7 for several radiation dosages. The characteristic frequency of the crossover from dc to high frequency is seen to increase with defect concentration. Owing to the peculiarities of the measuring circuit it was not possible to measure the irradiated samples at frequencies above 100 MHz. It appears that the conductivity in the high-frequency region, the saturation value, agrees with the saturation value obtained from the electric field measurements (see Fig. 5).

To investigate the effect of the defects on the

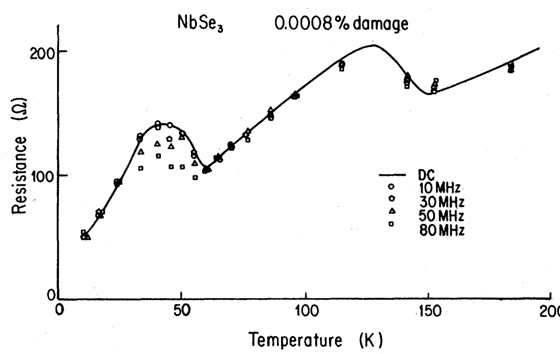

FIG. 5. Temperature dependence of the resistance of a slightly damaged sample for several frequencies.

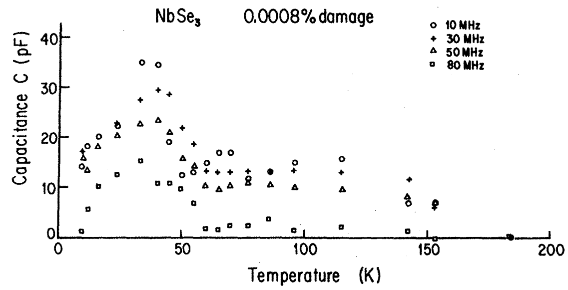

FIG. 6. Temperature dependence of the capacitance of a slightly damaged sample for several frequencies.

inverse of the dielectric constant and on the characteristic frequency, these two quantities are plotted as a function of the inverse residual resistance ratio in Fig. 8. The temperatures for all of the data shown corresponds to the resistivity maximum below T_2 measured separately for each sample. Our experiments show that this temperature is where the capacitance is maximum and the characteristic frequency and threshold field lowest. The characteristic frequency was chosen as the value where the conductivity was 20% through its transition from the low-frequency to the high-frequency value. This value was chosen due to the lack of complete transitions for the more highly doped samples. From the data it appears that the dielectric constant scales with one over the number of defects n_I. If one forces a power-law fit on the data for the characteristic frequency ω_C, the best fit occurs for $n_I^{1/2}$.

Without resorting to any particular model the data in Figs. 8 and 4 show a clear relationship between the threshold field and the inverse dielectric constant, both being linear in the defect concentration. Quite generally the dielectric constant is inversely proportional (at low fre-

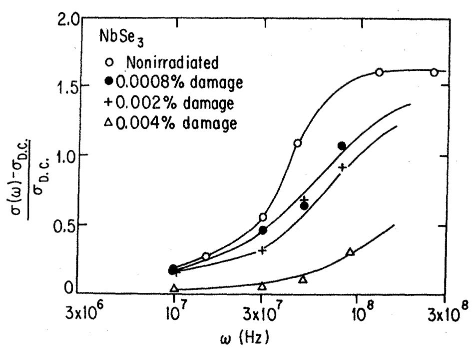

FIG. 7. Normalized conductivity change as a function of frequency for several radiation dosages. The temperature of each sample was taken at the point where E_T was minimum

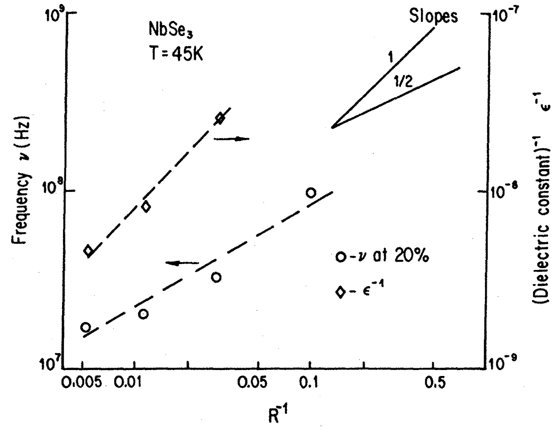

FIG. 8. Inverse-resistivity-ratio dependence of a characteristic crossover frequency from low- to high-frequency behavior and of the inverse dielectric constant which measured a restoring force.

quencies) to a restoring force acting on bound charges. The proportionality with the threshold fields indicates that this force is what must be overcome to get the nonlinear conductivity or to free the bound charges.

In pure $NbSe_3$ it has been seen that an overdamped harmonic oscillator can describe the frequency-dependent motion of a CDW (Longcor[13] and Grüner *et al.*[8]). The pinning force in this model is given by a spring constant K, which pins the CDW to a given site. If there were n_I pinning sites all with the same force constant, the total effective force constant would be $n_I K$. This means that the pinning frequency $\omega = \sqrt{k/m}$ should increase as the square root of the number of impurities.

If the characteristic frequency we measure is equal or proportional to the pinning frequency and the threshold field is proportional to E_0 (the characteristic field used in a Zener tunneling description of the nonlinear conductivity), then our findings are in agreement with the theory of Bardeen which predicts $E_0 \sim \omega_0^2$.[10] This result assumes that the entire CDW tunnels across small gaps caused by pinning.

However, the characteristic frequency measured in these experiments is not the pinning frequency but the crossover frequency $\omega_0^2 \tau$. This crossover frequency would be expected to increase here less rapidly than n_I due to the reduction of τ, the scattering or viscous damping time.

Within this model one would expect the threshold field for depinning a CDW to increase as the force constant, this leads to $E_T \sim n_I$. This model leads to a dielectric constant given by

$$\epsilon = 1 + \frac{4\pi Q^2}{M(\omega_0^2 - \omega^2 + i\omega_c^2)} . \quad (1)$$

For small frequencies $\epsilon \sim 4\pi Q^2/M\omega_0^2 \sim 1/n_I$ and thus $\epsilon \sim 1/n_I$, which is what was observed. The harmonic oscillator predicts a zero dc conductivity. This is because the normal electrons are not included in this simple model. The conductivity predicted by the harmonic oscillator model is one that is peaked at ω_0 unless the oscillator is overdamped. The work of Grüner *et al.*,[8] as well as the present study, indicate that the motion *is* overdamped. However, the effect of the impurities on the dielectric constant and threshold field is well described by the oscillator model whether damped or undamped.

In an attempt to include the normal electrons as well as the CDW Grüner *et al.*[8] used the model depicted in the insert of Fig. 7 which is easily derived in terms of an overdamped oscillator for the CDW. This says that there are normal electrons conducting in parallel to the CDW. The normal electrons are represented by a capacitance C and a resistance R_S. The conductance of this circuit is given by $1/\mathrm{Re}(Z)$, where Z is found from

$$\frac{1}{Z}=\frac{1}{R_N}+\frac{1}{R_S+1/i\omega C}\,. \tag{2}$$

This leads to a frequency-dependent conductance K of

$$K=\frac{1+\omega^2C^2(R_S+R_N)^2}{R_N[1+\omega^2C^2R(R+R_N)]}\,. \tag{3}$$

For low frequency $K\ (\omega=0)=1/R_N$; in other words, just the normal electrons contribute. For K $(\omega\to\infty)$ one obtains $1/R_N+1/R_S$. The conductivity rises smoothly between these values. However, in this single capacitor model it rises fairly rapidly. By including a distribution of C's corresponding to a variety of pinning energies a broader transition can be obtained.

To look at the dependence of the frequency on n_I one can look at the resistance of the circuit at the point where the system is 20% of the way between $R(0)$ and $R(\infty)$, since this was the value plotted in Fig. 8. Equating this value to Z in Eq. (2) gives

$$\omega_{1/5}=\frac{1}{2C(R_S+R_N)}\ . \tag{4}$$

Now if $C\sim 1/n_I$ as was seen experimentally one can calculate the limits for the dependence of ω on n_I. This is done by saying that either (a) $R_N, R_S \sim n_I$ or (b) R_N, R_S are independent of n_I. The actual result should be somewhere between these limits with the latter more appropriate as phonon scattering dominates. For the former case ω is independent of n_I, in the latter $\omega \sim n_I$. The observed dependence is less rapid than linear in n_I.

In conclusion we have shown that radiation damage produces very different behavior than substitutional impurities in $NbSe_3$. Whether these differences are due to weak versus strong pinning or inhomogeneous versus homogeneous disorder or small local shifts in the Fermi energy for the substitutional case are not yet known. Substitutional impurities increase the characteristic field for nonlinearity (E_0 and E_t) as n_I^2, while radiation damage produces a linear increase with defect concentration. Large dosages of radiation do not destroy the CDW while substitutional impurities (either isoelectronic or charged) do, as evidenced not only by the resistive anomalies but by the thermopower and superconductivity as well.[11,12]

The damage studies show that the inverse of the dielectric constant and the threshold electric field are proportional to one another and to the defect concentration. This indicates that both are measuring the pinning force on the CDW. The frequency-dependent conductivity shows a characteristic crossover frequency between high- and low-frequency saturation values which increases as the defect concentration increases. The characteristic frequency varies less than linear with defect concentration.

The total change in the conductivity from low to high electric field strength and from low to high frequency appears to be the same for small dosages as in the case for pure samples. However, the high-field conductivity values do not saturate to the values extrapolated from above the CDW transition as in pure samples. The high-field CDW state is lower in conductivity than the undistorted state.

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