Electron-beam irradiation effects on the charge-density-wave superlattice of $K_{0.30}MoO_3$

C. H. Chen, L. F. Schneemeyer, and R. M. Fleming
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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The formation of a charge-density-wave (CDW) superlattice in the blue molybdenum oxide bronze $K_{0.30}MoO_3$ is found to be extremely sensitive to electron-beam irradiation. Short exposure of the samples to an electron beam completely destroys the CDW superlattice whereas the underlying main lattice remains largely intact. The radiation damage in the CDW superlattice is believed to be electronic in origin.

Recently it was shown[1] that the blue bronze $K_{0.30}MoO_3$ exhibits non-Ohmic behavior at temperatures below a metal-semiconducting phase transition at 180 K which is similar to that observed in $NbSe_3$ and related compounds even though the structure of $K_{0.30}MoO_3$ differs considerably in detail from that of $NbSe_3$. Recent x-ray scattering experiments indicate that $K_{0.30}MoO_3$ has an incommensurate charge-density wave (CDW) which forms at 180 K (Ref. 2) and an incommensurate-commensurate transition which occurs at 110 K (Ref. 3). The wave vector of the CDW in the commensurate phase has been determined to be[3] $q = 0\vec{a}^* + 0.25\vec{b}^* + 0.5\vec{c}^*$. In the incommensurate phase the CDW wave vector is only incommensurate along $\vec{b}^*$. Strandlike domain structure associated the CDW phase transition in $NbSe_3$ (Refs. 4 and 5) and TaS_3 (Ref. 6) was reported recently using superlattice dark field transmission electron microscopy (TEM). TEM studies reveal that strands approximately 200–300 Å in width were arranged parallel to the conducting chain axis. It was also noted that the strandlike domains exhibit time-dependent contrast or a "twinkling" effect with an individual strand lighting up, branching, or vanishing in fractions of a second. The physical origin of the strandlike domains and the twinkling effect is still not understood at present.

Motivated by the similarity of CDW's between $K_{0.30}MoO_3$ and $NbSe_3/TaS_3$, we set out to investigate the CDW domain structure in $K_{0.30}MoO_3$, hoping that what we learn in $K_{0.30}MoO_3$ can shed some light on the understanding of domain structure observed in $NbSe_3$ and TaS_3. However, the investigation was plagued by the extreme sensitivity of the CDW to the high-energy electron-beam irradiation. On this note, we report our studies of the radiation damage in the CDW state of $K_{0.30}MoO_3$ and its related compounds.

Single crystals of the blue bronzes $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$ were obtained by the electrolytic reduction of a $(K, Rb)_2MoO_4$-MoO_3 melt. Crystals are platelets parallel to the $(\bar{2}01)$ cleavage plane with b as the rapid growth direction. Thin samples for TEM were obtained by cleavage of bulk crystals parallel to the $(\bar{2}01)$ cleavage plane. Acceleration voltages of 60, 100, 150, and 200 kV were used in the present study.

As mentioned earlier superlattice peaks have been observed by x-ray scattering at $0\vec{a}^*$, $0.25\vec{b}^*$, and $0.5\vec{c}^*$ in the commensurate CDW state. Surprisingly enough, we failed to see any CDW superlattice spots by electron diffraction in our initial attempts. Since electrons scatter much more strongly than x-ray photons, it is particularly perplexing that CDW superlattice reflections cannot be observed in the electron diffraction pattern. The absence of superlattice reflections leads us to suspect the electron-beam-irradiation

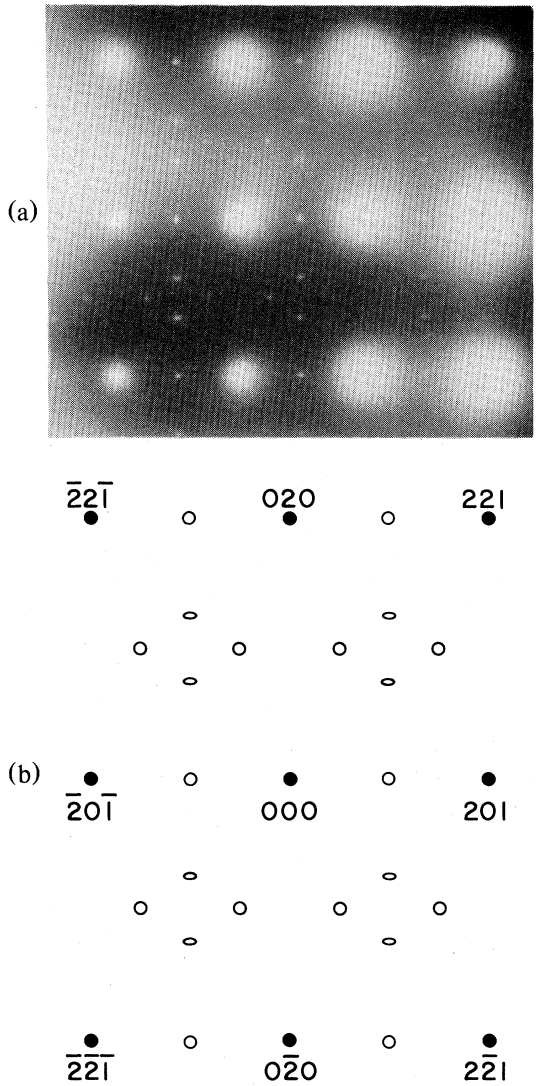

FIG. 1. (a) Electron diffraction pattern recorded during the presence of CDW superlattice reflections. (b) is a sketch of main features shown in (a). The crystal was positioned in such a way that the Ewald sphere cuts through a reciprocal plane defined by $\vec{b}^*$ and (201) reflections.

damage to the superlattice. To avoid any radiation damage prior to the formation of CDW's, the sample was cooled down below the incommensurate-commensurate transition temperature before the electron beam was turned on. This is contrary to the customary practice in which one usually examines the quality of the sample before it was cooled down. Once the low temperature is reached, the sample is moved away from the path of the electron beam and the electron beam is then turned on. The CDW superlattice spots should be directly observable in a reciprocal plane defined by $\vec{b}^*$ and (201) reflections as suggested from x-ray diffraction studies. A small area ($\sim$ a few micrometers) of the sample is then used to set up the desired diffraction condition. The electron beam is brought near crossover ($\sim$ a couple of micrometers in size) to minimize the area of damage. Once the desired diffraction condition is obtained, fresh sample areas are moved into the electron beam and CDW superlattice reflections located in the expected areas are observed in the diffraction pattern. However, the superlattice is found to be relatively short-lived—their intensity fades and disappears under the irradiation of the electron beam in a few seconds. A glance of the CDW superlattice reflections before they completely disappear is shown in Fig. 1(a). A sketch of the main features in the diffraction pattern is also shown in Fig. 1(b). From Fig. 1 we can clearly see a pair of CDW reflections that occur near the forbidden (111) reflections with a wave vector $0\vec{a}^*$, $0.25\vec{b}^*$, and $0.5\vec{c}^*$ in agreement with the x-ray result. Moreover, Fig. 1 also reveals that diffuse streakings appear in a direction perpendicular to the $\vec{b}^*$ axis before the superlattice reflections completely fade away. This implies that the lateral coherence length of the CDW's on the potassium chains has been drastically reduced by the radiation damages induced by the irradiating electron beam. Note that there are no significant changes of the diffraction spots of the underlying main lattice after prolonged electron-beam irradiation. It appears that the damage shows up most dramatically only in the CDW superlattice. We also note that the damage created is permanent and the annealing of the sample at room temperatures does not rejuvenate the appearance of the superlattice at low temperatures. Damage can also be induced at room temperature and this is why we were not able to see any superlattice at all in initial experiments when the sample was examined at room temperature before it was cooled down.

It should be noted that the above observations were made with 200-kV electrons. Radiation damage due to the elastic collision process might be possible in this case. To prove the origin of the radiation damage we have carried out similar observations with 150-, 100-, and 60-kV electrons. The CDW superlattice reflections are again found to be relatively short lived in these cases just as that observed when 200-kV electrons were used. This observation suggests that the radiation damage is electronic in origin. This means that electronic excitations are created by the incoming high-energy electrons, and as a result of electronic deexcitation the energy is transferred to the lattice and elastic collision process then takes place. The fact that the same damage can occur at room temperature and low temperature indicates that the electronic excitation has a relatively long lifetime even at room temperature. Radiation damage has also been observed in other CDW systems such as $NbSe_3$ (Ref. 6). However, in the case of $NbSe_3$, radiation damage to the CDW superlattice only occurs at low temperatures.

We have also made observation of the CDW superlattice reflections in other materials that belonged to the same family such as $Rb_{0.3}MoO_3$. Again, CDW superlattice spots are short-lived under the irradiation of the electron beam. Some attempts to stabilize the CDW superlattice in $K_{0.30}MoO_3$ have also been made by doping with a few parts per million Fe. By doing this, we are hoping CDW's can be more strongly pinned at the impurity Fe site and therefore become less susceptible to the radiation damage. It turns out that this impurity doping scheme does not increase the lifetime of the CDW superlattice in any significant way.

In conclusion, we have found that the CDW superlattice in $K_{0.30}MoO_3$ and its related compounds are relatively short-lived under the irradiation of the electron beam due to the creation of radiation damage which is believed to be electronic in origin. The details of the damage are largely unknown. However, the damage is believed to be quite similar in many ways to the defect structure of the color centers observed in many alkali halides and the recombination-enhanced defect processes in semiconductors. The short lifetime of the superlattice makes the real-space imaging the CDW domain and/or discommensuration structure extremely difficult if not impossible.

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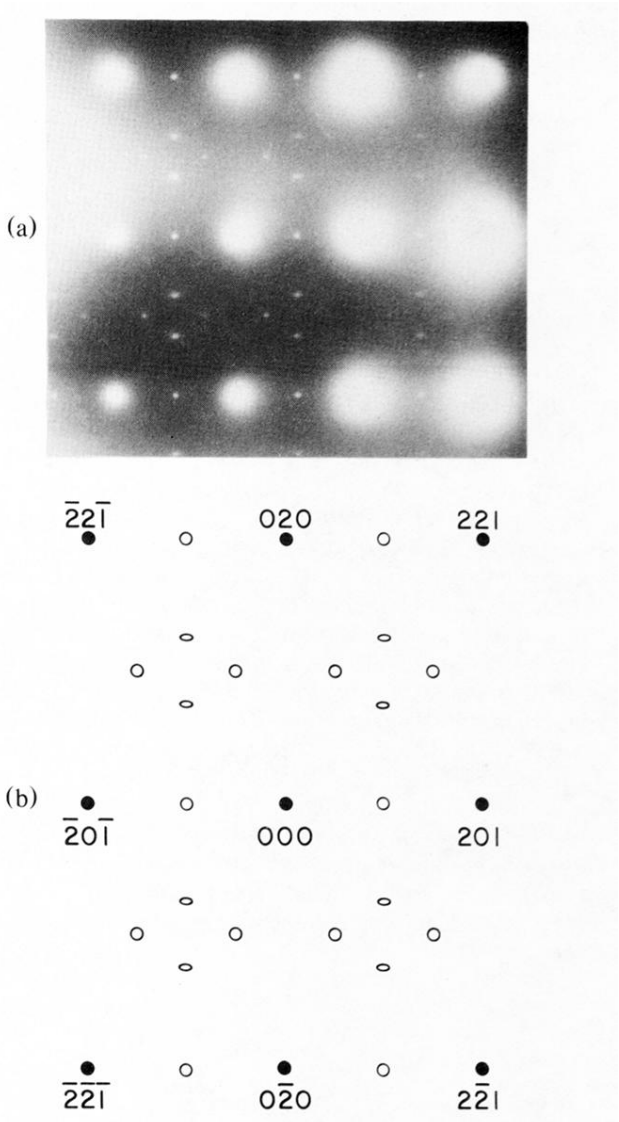

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