Current controlled negative differential resistance behavior in Co$_2$FeO$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$ single crystals

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$I$–$V$ curves showing negative differential resistance (NDR) are reported for single crystals of Co$_2$FeO$_2$BO$_3$ at 315 K and 290 K and for Fe$_2$O$_2$BO$_3$ at 300 K, 260 K and 220 K. Resistivity measurements are presented for both systems, parallel and perpendicular to the $c$ axis, in the range 315–120 K. The high hysteretic behavior of the $I$–$V$ curves in Co$_2$FeO$_2$BO$_3$ around room temperature is discussed and the heat dissipated is estimated, suggesting an increase in the sample temperature of almost 22 K for the $I$–$V$ curve at 315 K and a dominant contribution of Joule self-heating for the observed NDR. In contrast, insignificant hysteresis is observed on the $I$–$V$ curves of Fe$_2$O$_2$BO$_3$ around room temperature. The depinning of charge order domains is suggested as the main contribution to the NDR phenomenon for Fe$_2$O$_2$BO$_3$. The high reproducibility of the NDR in the Fe$_2$O$_2$BO$_3$ single crystal allows its use as a low frequency oscillator, as it is demonstrated.

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1. Introduction

The observation of current controlled negative differential resistance was reported in several systems for different ranges of temperatures, with Joule self-heating being the most accepted explanation of the NDR phenomenon. The increase of the current implies in a power increase in the sample and a consequent generation of heat. If the resistivity of the sample decreases when the temperature is increased, the heat drives the system from a high to a low resistivity state with the increase of the current and current controlled NDR is observed.

Alexandrov et al. [1] have developed a model to explain current controlled NDR in Ti$_2$O$_3$ menristor. They used a thermal activation law for small polarons mobility and Ohm’s law to write parametric equations for voltage and current as a function of power. Current controlled NDR was also observed in the Kondo insulator SmBi$_3$ in the range 2–10 K [2]. The authors have also attributed the effect to Joule self-heating. However, they state that there is a nonlinear resistance in the current and voltage relationship. Nonlinear conduction was also observed in the current controlled $I$–$V$ curves showing NDR in single crystals of the organic conductor (TMET-TTP)$_4$PF$_6$ in the approximate range 50–202 K by Mori et al. [3]. Using a phenomenological thermal approach, the authors found a very low value of specific heat when the experimental data was fitted, allowing them to conclude for the unimportance of Joule heating. Nonlinear conduction has also been found in the current controlled $I$–$V$ curves in single crystals of Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ observed in the charge order (CO) state that takes places below 240 K [4]. NDR was only observed below 170 K for the range of currents applied in the experiment. They have concluded that heating is not the cause of NDR but has some effect at high currents. In a similar way, Asamitsu et al. [5] have concluded that the changes in resistivity states in Pr$_{0.7}$Ca$_{0.3}$MnO$_3$ were not due to simple thermal effects.

Current controlled NDR curves observed around room temperature in single crystals of the oxy-borates Co$_2$FeO$_2$BO$_3$ and Fe$_2$O$_2$BO$_3$ are reported in this work. We aim to emphasize the differences observed in the NDR curves of these similar materials and their possible explanations. Both are compounds with the ludwigite M$_2$MO$_2$BO$_3$ chemical formula (M being a transition metal ion) and an orthorhombic $Pbam$ structure. They are formed by substructures, which consist of three leg ladders (3LL) along the crystallographic c axis direction. These 3LL are composed by oxygen octahedra having transition metal ions at their centers. The projection of the whole structure in a plane perpendicular to the c
axis is shown in Fig. 1 (lower inset). The boron ions, in trigonal coordination, bind these substructures together. In Co$_2$FeO$_2$BO$_3$, the 4 and 2 sites are occupied by iron ions while cobalt ions occupy sites 1 and 3 [6–8]. In the case of Fe$_2$O$_2$BO$_3$, while the iron ions at sites 3 and 1 are divalent, those at sites 4 and 2 are almost trivalent and can be seen as formed by a background of Fe$^{3+}$ ions with one extra electron for every three ions. The Fe$_2$O$_2$BO$_3$ is a unique system in the family of the ludwigites. X-ray diffraction measurements [9] have shown that this material has a structural transition at 283 K, which doubles the lattice period along the c axis. Around 304 K a broad minimum is seen in the c axis resistivity of Fe$_2$O$_2$BO$_3$ which could mark the charge order transition, as Mossbauer spectroscopy has found $T_C$ around 300 K. However, a definitive assignment was complicated by the fact that this transition is thermal history dependent and was observed for some, but not all the measured samples. In polycrystalline Fe$_2$O$_2$BO$_3$, both Mossbauer spectroscopy and resistivity, could identify the charge order transition around the same temperature, in that case $T_C\sim 317$ K [13]. For Co$_2$FeO$_2$BO$_3$ features in the resistivity were clearly observed at some temperatures in both directions, marking differences in the temperature dependence. However, a charge order transition has not been detected by X-rays diffraction in this compound and it lacks information obtained by local techniques, thus, we could not make any attribution of those features in resistivity.

In Fig. 2, I–V curves showing NDR are displayed for Co$_2$FeO$_2$BO$_3$ at 315 K (blue circles) and 290 K (red squares). Both curves show hysteresis. The resistance at 290 K is larger than that at 315 K as can be taken from the I–V curve. The enclosed areas are the dissipated power, which can be obtained by integration. The times to take each curve were recorded and the amount of heat dissipated was 19.1 mJ and 24.8 mJ for the 290 K and 315 K I–V curves (positive current run), respectively. The specific heat is available for both samples up to 230 K for Fe$_2$O$_2$BO$_3$ and 275 K for Co$_2$FeO$_2$BO$_3$ [7] being 177.8 J mol$^{-1}$ K$^{-1}$ and 137.6 J mol$^{-1}$ K$^{-1}$ respectively. These values correspond respectively to 79% and 61% of the Dulong and Petit limiting value of the specific heat per mole around room temperature:

$$C = 3nR$$

R is the gas constant and n is the number of atoms per unit formula, in both cases here n=9. It is assumed that at 315 K the Dulong and Petit value of Eq. (1) corresponding to a value per mole of 225 J K$^{-1}$ has been reached at 315 K. In this case, the estimated heat capacity of the Co$_2$FeO$_2$BO$_3$ sample (1 mg) is 0.85 mJ K$^{-1}$ and the amount of heat of 24.8 mJ can be obtained with a final temperature $T_f$ given by:

$$Q=0.85\text{mJ}\text{K}^{-1}\int_{315\text{K}}^{T_f} dT$$

Using the heat dissipated obtained previously, Eq. (2) gives a value of $T_f=337$ K for the final temperature attained by the sample
Fe$_3$O$_2$BO$_3$ showing NDR. Inset: details of the 260 K and 300 K curves showing (blue triangles), 260 K (black squares) and 300 K (red circles) for single crystals of gend, the reader is referred to the web version of this article.)

Unlike 300 K (red circles), 260 K (black squares) and 220 K (blue triangles) and 315 K (blue squares) for single crystals of Co$_2$FeO$_2$BO$_3$ showing NDR. However, this situation is not found on the heating can indeed be the most important or maybe the only cause of NDR in Co$_2$FeO$_2$BO$_3$. Nevertheless, the specific heat of Fe$_3$O$_2$BO$_3$ tends to the same Dulong and Petit value at room temperature, the sample mass is even smaller than that of the Co$_2$FeO$_2$BO$_3$ single crystal and the resistivity is also activated in this same temperature range. These facts point to another dominant mechanism of NDR for Fe$_3$O$_2$BO$_3$ that takes place before any significant amount of heat has been dissipated.

In the search for such a mechanism, it is important to note the similarities of the Fe$_3$O$_2$BO$_3$ I–V curves and those observed for Pr$_{0.63}$Ca$_{0.37}$MnO$_3$ in Ref. [4]. Besides, both systems are mixed valence materials, in the case of Fe$_3$O$_2$BO$_3$, having Fe$^{3+}$ and Fe$^{2+}$ ions, and Mn$^{3+}$ and Mn$^{4+}$ in Pr$_{0.63}$Ca$_{0.37}$MnO$_3$. Both have charge ordered states. In both, the NDR phenomenon appears in the charge ordered state, is reproducible, and has small power dissipation. In Ref. [4], some possible mechanisms to explain NDR were suggested. First, the creation of conductive paths as the current increases, but in this case the reproducibility seen in the I–V curves seems unlikely. Second, that NDR is due to the depinning of the charge order domains above a threshold applied field. This possibility would help to understand why NDR is observed in the charge ordered state and disappears as a magnetic field of 8 T melts the charge order state into a ferromagnetic state. NDR has also been observed near 40 K in the prototypal charge-density wave (CDW) system NbSe$_3$ [14] above the threshold field for nonlinear conduction. Evidence of the significant contribution to the conductivity due to the depinning of these charge ordered domains emerge from those observations, reinforcing the possibility of observing NDR without significant Joule heating. The depinning of CDW systems was studied in linear chains compounds; see G. Grüner [15] for a review. In the specific case of Fe$_3$O$_2$BO$_3$ above a current threshold, which according to careful measurements performed for very low applied currents seems be around 0.3 $\mu$A, with a change of I–V behavior from linear to nonlinear, the CO collective state pinned by impurities becomes depinned and contributes to the total conductivity. The I–V curve reflects the two contributions, the single-particle linear contribution, and that of the depinned CO domains. The CO contribution to the conductivity increases with the increase of the current in a nonlinear way and overcomes the single-particle contribution for the conductivity for the range of currents NDR is observed.

Next, the application of a single crystal of Fe$_3$O$_2$BO$_3$ in an oscillator, as already known for systems that display NDR, like semiconductor devices, is described. The circuit used to drive low frequency oscillations in the sample is shown in Fig. 4a. Initially, we assume that the total current given to the circuit is larger than the current corresponding to the maximum voltage in Fig. 3. It splits in two components, one that charges the capacitor and other that passes through the sample. When the capacitor is charged all the current passes through the sample and, as it is driven to the NDR region, its potential decreases becoming smaller than the single-particle contribution. Current can be driven again to the capacitor and a new charging cycle begins. The charging time depends on the current value and the total charge is given by the voltage (for a fixed capacitance). In Fig. 4b and c oscillations are shown applying current perpendicular to the c axis at 230 K and 300 K respectively. The oscillations can be driven at room temperature by a voltage of only 3 V.

**4. Conclusions**

In this work, we have presented I–V and resistivity data from two oxy-borates single crystals, Co$_2$FeO$_2$BO$_3$ and Fe$_3$O$_2$BO$_3$, which exhibit current controlled negative differential resistance phenomenon in the room temperature range. They have the same orthorhombic Pbam structure, similar values of room temperature
specific heat and thermally activated resistivities around this temperature. In the case of Co$_2$FeO$_2$BO$_3$, a large hysteresis was observed on the I–V curves showing NDR. The amount of heat generated was quantified and Joule self-heating was identified as the main mechanism of NDR in Co$_2$FeO$_2$BO$_3$ single crystals. On the other hand, the lack of significant hysteresis on the I–V curves of Fe$_3$O$_2$BO$_3$ requires another mechanism for the observed NDR phenomenon besides Joule self-heating. The Fe$_3$O$_2$BO$_3$ system is the only system in the family of ludwigite oxy-borates that shows a structural transition associated with the formation of a transverse charge density wave. Consequently, it is natural to attribute the difference of the observed NDR phenomenon in Fe$_3$O$_2$BO$_3$ and Co$_2$FeO$_2$BO$_3$ to the existence of a CO in the former. Furthermore, the depinning of charge ordered domains is the dominant mechanism of NDR in Fe$_3$O$_2$BO$_3$ single crystals. It takes place before any significant amount of heat is dissipated, allowing very reproducible NDR curves to be obtained. This high reproducibility made possible the application of a Fe$_3$O$_2$BO$_3$ single crystal in a low frequency oscillator, which could be driven at room temperature by a voltage of only 3 V.

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