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Anomalous effects of repeated martensitic transitions on the transport, magnetic and thermal properties in Ni–Co–Mn–Sb Heusler alloy

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Abstract

The detrimental effects of repeated thermal/field cycling across the martensitic transition on the transport, magnetic and thermal properties of $Ni_{45}Co_5Mn_{38}Sb_{12}$ are studied. With the help of resistivity and magnetization measurements, it is shown that the resistivity increases and the magnetization decreases monotonically with continuous temperature or field cycling across the martensitic transition. It is also found that the martensite to austenite transition temperature increases with repeated structural change. The changes occurring in these physical properties are seen to be irreversible in nature. The possible changes in the lattice and the microstructure by repeated structural change seem to be responsible for the observed variations.

Keywords: Thermal/field cycling; Martensitic transition; Magneto-structural transition; Heusler alloy

1. Introduction

The first-order magneto-structural transition has been a subject of special interest among researchers in the last few years. Magnetic systems such as Gd_5Ge_4 [1], MnAs [2] and some manganites showing colossal magnetoresistance [3,4] have been widely studied owing to the existence of coupled ferromagnetic (FM) to antiferromagnetic (AFM) transition and the structural phase transition. As a consequence of this magneto-structural transition, a giant magnetocaloric effect and large magnetoresistance have been observed in these materials [2,3,5]. Another characteristic feature of these materials is that the first-order phase transition can be induced by magnetic field. It is observed that, at a critical temperature and above a critical field, this field-induced transition gives rise to large irreversibility on the field variation of resistivity [3]. Among all the intermetallic compounds showing first-order magneto-structural transition, $Gd_5(Si_xGe_{4-x})$ has received considerable interest, as it shows a variety of anomalous behavior in the physical properties. The crystallographic phase transition in this alloy has been understood by invoking the martensitic scenario for the phase transition [6]. It is observed that, by repeatedly inducing the structural transition by temperature cycling, the electrical resistivity increases monotonically in each cycle, which is attributed to structural disorder [7–9].

Another important system in the family of materials showing magneto-structural transition is the Heusler alloys, which undergo a martensitic transition. These alloys undergo a martensitic transition from high temperature austenite phase (cubic) to low temperature martensite phase (orthorhombic or tetragonal). As this transition is coupled with the magnetic state, a significant change in the magnetic state between the two crystallographic phases is observed. Owing to this martensitic transition, a large

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shape memory effect [10,11], giant magnetocaloric effect [12–15] and large magnetoresistance [16,17] have been observed in these alloys. The martensitic transition can be tuned by application of field and by chemical or hydrostatic pressure [18–20]. In a recent work it was observed that, under appropriate conditions, the high field austenite phase gets arrested, resulting in a large irreversibility in the field dependence of magnetization, resistivity and heat capacity [21]. These results reveal that the irreversibility obtained in this system is a consequence of first-order martensitic transition. Therefore, it is important to study the effect of the martensitic transition in detail on the physical properties of the system.

The irreversibility in the resistivity data indicates that there must be some local disorder arising in the sample because of the change in the crystal structure. The change in the crystal structure modifies the magnetic and electronic states of the system. This effect can become more significant if the two crystal structures possess different microstructures. This difference may create microcracks which hinder the electron transport [22]. In the present case, the martensitic plates are formed in the martensite phase, whereas there are no such plates in the austenite phase [23,24]. Another important fact is that the atomic size difference and thermal fluctuations in a crystal lattice can affect the atomic displacement, which may change the atomic order parameter, giving rise to a change in resistivity [25]. In an off-stoichiometric alloy such as $Ni_{50}Mn_{25+x}Sb_{25-x}$, the extra Mn atoms occupy the Sb site, which gives rise to a large size mismatch. The extra Mn atoms occupying the Sb sites couple antiferromagnetically with the Mn in regular Mn site. The AFM interaction becomes more prominent in the martensite phase, owing to the decrease in Mn–Mn distances [26].

It is of interest to probe how these factors change when the alloy is subjected to repeated structural changes, as a rearrangement of the atomic position is needed each time the alloy undergoes a structural change. Therefore, this paper studies the effect of repeated structural transitions induced by temperature and field cycling across the martensitic transition in the $Ni_{45}Co_5Mn_{38}Sb_{12}$ Heusler alloy. The changes occurring due to the repeated martensitic transition were revealed by the temperature and field dependence of resistivity, magnetization and heat capacity data.

2. Experimental details

The method of sample preparation is reported in Ref. [15]. The structural details of the sample have been mentioned elsewhere [27]. The magnetization (M) measurements were performed using a vibrating sample magnetometer attached to a physical property measurement system (PPMS; Quantum Design, PPMS-6500). The electrical resistivity (ρ) measurements were carried out by the linear four probe method using PPMS. The heat capacity (C_P) was also measured using the PPMS. In the temperature and field cycling of resistivity and magnetization measurements, the data were taken in every cycle and, for clarity, only the data corresponding to certain cycles are shown in the figures. All the temperature cycling data were taken in the heating mode. Different pieces of samples were used for resistivity, magnetization and heat capacity measurements. The microstructure of the samples was studied by optical microscopy (OM). For this, the samples were polished and then etched in a solution containing methyl alcohol and nitric acid in a 10:1 ratio.

3. Experimental results

In Fig. 1, the temperature variation of resistivity measured in zero and 50 kOe fields is shown. The measurements were performed in both cooling and heating modes. In both zero and 50 kOe curves, the data were first collected in cooling mode and then in heating mode. On heating, the martensite to austenite transition is followed by a large decrease in resistivity. The hysteresis between the heating and the cooling curves signifies the first-order transition. The high resistivity of the martensite phase may be due to the plate type of microstructure, the presence of microcracks, which releases internal stress leading to a higher resistance [28]. In the zero field curve, it is observed that the resistivity of the heating curve ends with a higher value than the starting value of the cooling curve. In the 50 kOe curve, the martensitic transition occurs at a lower temperature than that in the zero field. Another interesting feature observed from Fig. 1 is that the 50 kOe curve follows a higher resistivity path than the zero field one throughout the martensite phase, giving rise to an anomalous positive magnetoresistance. The authors mention here that they have recently reported the resistivity variation in the same alloy in zero field and in 50 kOe [29]. It was found that the effect of field on the resistivity data throughout the martensitic phase is quite negligible, which is in disagreement with the data presented in the present paper (Fig. 1). The two data correspond to two different batches of samples, prepared with different batches of Mn. Therefore, the difference in the resistivity

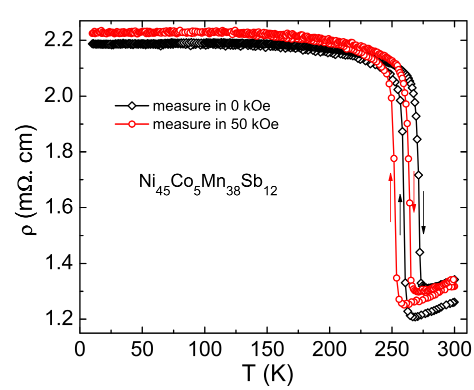

Fig. 1. Temperature dependence of resistivity measured in heating and cooling modes in zero (circles) and 50 kOe (squares) fields in $Ni_{45}Co_5Mn_{38}Sb_{12}$.