Insulator-Metal Transition in Highly Compressed NiO

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Insulator-metal transition in highly compressed NiO

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Abstract

The insulator-metal transition was observed experimentally in nickel monoxide NiO at very high pressures of ~240 GPa. The sample resistance becomes measurable at about 130 GPa and decreases substantially with the pressure increase to ~240 GPa. A sharp drop in resistance by about three orders of magnitude has been observed at ~240 GPa with a concomitant change of resistance type from semiconducting to metallic. This is the first experimental observation of an insulator-metal transition in NiO anticipated by Mott decades ago. From simple multi-electron consideration the metallic phase of NiO forms when the effective Hubbard energy, U_{eff}, is almost equal to the estimated full bandwidth 2W.

A transition of an insulator into a metallic state is a general fundamental phenomenon related to a broad range of physical systems [1-6]. Nickel monoxide - NiO - is historically one of the first compounds, which was involved in the understanding of strongly correlated electronic systems. The importance of observing and understanding the insulator-metal transition in compressed NiO for condensed matter physics (correlated electron physics) ranks close to the metallization of hydrogen under pressure. Pioneering studies by Mott and co-workers treated NiO as a typical example of "Mott" insulator with a wide *d-d* energy gap U, which occurs due to strong Coulomb electron repulsion on the same Ni site [7-10]. Simultaneously, Mott predicted possible insulator-metal transition (IMT) in compressed NiO. Despite these first suggestions of metallic high-pressure phase of NiO by Boer, Verwey, Mott, and Peierls [11, 12], it is not known until now at what pressure will this material transform into a metallic state. Numerous theoretical studies gave contradictory predictions regarding pressure range and nature of IMT in NiO. It has been established since then that the Mott-Hubbard *d-d* energy U in NiO is comparable in magnitude to the *p-d* charge transfer energy Δ [13, 14], and nickel monoxide is situated on the borderline between the Mott insulator and charge transfer insulator regimes. However, recent resonant inelastic scattering experiments [15] indicate that the lowest energy gap E_g in NiO is related to the Mott-Hubbard electron transfer process between neighboring Ni sites.

Several preceding experimental and theoretical studies have tackled the problem of pressure effects on electronic correlations in simple oxides. The Mott transition is reportedly tightly interconnected with emergent superconductivity [16-18], but the theoretical understanding of the wealth of phenomena related to the transition still remains a challenge. Early theoretical LDA and GGA calculations by Cohen *et al* [19] predicted that band broadening effects are responsible for a magnetic collapse in simple oxides FeO, MnO, and CoO; in NiO a nearly second-order phase transition accompanied by magnetic collapse at 230 GPa was predicted [19]. Recent dynamic mean field theory calculations (DMFT) of MnO by Kunes *et al* [20] have demonstrated the importance of the spin-crossover effects which overcome Hund's exchange energy under pressure. Notably, it follows that the effective Hubbard energy U may be strongly dependent on pressure, which is at odds with predominant practice of considering U as nearly pressure independent parameter[21]. Pressure-dependent U values have been derived by Ovchinnikov [22, 23] within a simple theoretical framework that takes into account crystal field effects. This approach has been supported by extensive experimental results for Fe-based oxide materials [23, 24].

Here we report the observation of the insulator-metal transition in NiO. We find also that the lowest energy gap E_g of the insulating phase under pressure can be rationalized based on the pressure-dependent U, following simple predictions based on crystal field theory [22, 23].

Nickel monoxide is an antiferromagnetic insulator with a Néel point of 523 K at ambient pressure [25]. In one of the recent theoretical calculations [26] it was suggested that the transition to the metallic state should occur at very high compression ratio. The transition has been predicted at $(V_0\text{-}V)/V_0 \sim 0.4$ [26] from calculation using the Perdew-Wang generalized gradient approximation (PWGGA) functional and at $(V_0\text{-}V)/V_0 \sim 0.65$ [26] with the hybrid density functional (P3LYP) method. Based on these theoretical results, we have evaluated transition pressures from the known equation of state of NiO [26-28]. The P3LYP method predicts a very high pressure of metallization in NiO, at about ~1 TPa [26-28]. Notably, this calculation predicts the value of the energy gap at 4 eV [26], very close to the experimental value at ambient pressure. In contrast, the PWGGA method predicts a much lower metallization pressure of ~230 GPa [26-28]; however, the predicted optical gap of 0.7 eV [26] is far from the experimental value.

On the experimental side, the pressure of possible transition is expected to be above ~150 GPa. Recent x-ray diffraction experiments on the distorted rock-salt structure of NiO have found it stable up to a pressure of ~147 GPa [28], and the optical gap does not change up to ~80 GPa according to reported optical absorption measurements [27]. It has been established from analysis of the *d-d* optical transitions [27] that the crystal-field parameter $10Dq$ has a pressure derivative of about 7.28 meV/GPa. The pressure slope of the Neel temperature T_N has been determined as $\partial(T_N)/\partial P \sim 7.33$ K/GPa from two-magnon Raman scattering [21] and from differential thermal analysis [29] measurements. Thus there appears to be no experimental indication of pressure-induced metallization in NiO; all reported results are compatible with the persistence of a stable antiferromagnetic insulating state in NiO to the highest pressure reached experimentally until now. Since the reported theoretical and experimental studies suggest very high pressure of the insulator-metal transition in NiO, we have approached this important problem using multimegabar diamond anvil cell techniques.

Here we describe in brief the experimental procedure of resistivity measurements. We have used thin NiO single crystal samples in a thin platelet shape, or samples compressed to a platelet shape from powder, with thickness about or less than 1 micron. The samples with lateral dimensions 15-30 microns were placed directly on the cBN surface of a preindented cBN gasket [30] (no pressure medium); four thin Pt foil leads (thinner than 1 micron) were placed on the surface of the sample and were clamped by the opposite anvil (see Fig. 1). The pressure was measured by the standard ruby technique in the range 0-100 GPa, and from the high energy edge of a first order Raman peak of diamond at higher pressures [31]. According to our estimates from pressure gradient along the culet [32], the uniaxial stress was about ± 10 GPa at the maximum pressures achieved in the experiments. The additional details of the resistivity experiments are described elsewere [31-33] and in supplementary information.

We show the change in optical transparency of a NiO sample at the insulator-metal transition in Fig. 1. The sample is almost transparent at 35 GPa and is hardly distinguishable from the surrounding cBN gasket. A black part of the sample can be seen at about ~240 GPa, bridging between two of the four Pt leads. This is the metallic phase of NiO and it is located in the region of the highest compression [32]. The sample becomes more transparent away from the highest pressure region, as shown in Fig. 1(b).

The resistance of the sample becomes measurable at ~130 GPa. At higher pressures the resistance decreases strongly with pressure up to ~240 GPa and falls sharply by about three orders of magnitude at the transition pressure ~ 240 GPa. The pressure dependence of the resistance is shown in Fig. 1c . The sharp drop in resistance at the transition is clearly seen in the inset in Fig. 1c. We have performed several temperature scans of the resistance at different pressure points to confirm the metallic state at high pressures. For this purpose we used a custom designed diamond anvil cell that has a very high stability of pressure during cooling-warming cycles between liquid helium and room temperatures. This cell was developed based on our experience in building nonmagnetic miniature diamond anvil cells [34]. We show the resistance of NiO as a function of inverse temperature during pressure increase in Fig. 2(a). It is obvious that the observed temperature dependence is non-metallic, but also strongly nonlinear. Such nonlinear behavior is very similar to temperature dependencies of the resistance in Li-doped NiO crystals [10, 35]. The possible explanation of such non-linearity is in the nature of the charge carriers, which are believed to be "large polarons" [10, 35] in the *2p* band of oxygen (hybridized with the lower Hubbard d^8 band) at room temperature. However, at lower temperatures the mechanism of small-polaron hopping in the d^8 band may become effective, with smaller activation energy, and with dominating hopping conductivity at lower temperatures [10, 35]. It should be noted, that more complex conductivity patterns may come into play with more than one minor impurity species present in NiO samples [10, 35]. However, at the insulator-metal transition all these mechanisms would yield to a major change in the conductivity regime. In Fig. 2(b) we show the change in the temperature coefficient during the transition from the non-metallic to the metallic state at ~240 GPa.

To understand the pressure-induced behavior of the E_g, we have measured reflectivity spectra of NiO in the UV-VIS range, which are shown in Fig. 2(c). As a crude assumption, the value of the E_g was determined from the position of the peak in the UV reflectivity spectrum [36] (Fig. 2(c)) (More detailed analysis involving optical properties of the sample will be presented elsewhere). It is clear from Fig. 2(d) that the E_g is almost constant up to about 55 GPa, whereas above 55 GPa the E_g drops approximately linearly with a slope $\partial E_{opt}/\partial P = -5.0\ (\pm 0.3)$ meV/GPa. At the transition pressure ~240 GPa reflectivity peak position drops down sharply to a new, slightly lower value in the metallic phase stability range. This is clearly seein in the last two spectra, which are shown in Fig. 2(c). The energy decrease was about 0.2 eV. The pressure behavior of the E_g is compared to the behavior of thermal-activation energy (calculated at room temperature) in Fig. 2(d). While pressure behavior of the feature at 4 eV is compatible with the expected behavior of the Mott-Hubbard gap U-W, we leave its interpretation (both at ambient and at high pressure conditions) open for discussion, because it needs a better theoretical understanding not available at this moment.

The value of the activation energy is much less than one half of the E_g, which means that the conductivity in NiO is most probably due to minor impurities. The pressure derivative of the thermal-activation energy is equal to $\partial E_{ac}/\partial P = -0.32 \pm 0.05$ meV/GPa, which gives a relative slope similar to the E_g $1/E_{ac}\cdot(\partial E_{ac}/\partial P) \sim 1/E_g\cdot(\partial E_g/\partial P)$. The thermal activation energy drops abruptly and the resistance shows metallic-like temperature dependence at the insulator-metal transition.

We offer a brief discussion of our results based on a simple theory that takes into account crystal field effects [22, 23]. It is generally believed that a Mott transition occurs when the effective Hubbard parameter is nearly equal to the total d^8 bandwidth, or $U_{\text{eff}} \sim 2W$. For Mott-type IMT, a more accurate analysis shows that at the transition

$$U_{eff} \approx x \cdot W \tag{1}$$

where $\boldsymbol{x}$ depends on the crystal lattice, the particular band structure (single-particle density of states), and the approximations used to approach this problem. The first solution suggested by Hubbard gives $\boldsymbol{x} \sim 1.74$ [37], but the DMFT calculations [38] give two critical concentrations $\boldsymbol{x_1} \sim 2.6$ (limiting pure metal solutions), and $\boldsymbol{x_2} \sim 3.3$ (limiting pure insulating solutions). At finite temperatures, insulating and metallic phases will coexist in the region $2.6<x<3.3$, and the insulator-metal transition is of first-order type [38]. Presumably, the IMT in NiO should be accompanied by an iso-structural transition of the first-order type with possible large volume drop [38]. In this case, the transition should proceed through the nucleation of the new phase coexisting at the same pressure with the low- pressure phase due to large energy barrier between high- and low- pressure phases. This picture is supported by theoretical computations [26] when low- and high- pressure phases coexist in the wide range of Mott-Hubbard gap to the bandwidth ratio: 2.6<x<3.3 [26], and by our observation of a pressure drop at the sample position after the transition [32].

To estimate parameter ***x*** at high pressure for NiO we have used recent experimental and theoretical evidence pointing to the significant role played by spin crossover effects in phase transformations and electronic transitions in $3d^n$ metal oxides [22-24]. For the Ni^{2+} ion with d^8 configuration, the simple multi-electron consideration [22, 23] predicts that the effective Mott-Hubbard energy $U_{\mathrm{eff}} = U(\mathrm{d}^7)+U(\mathrm{d}^9)-2U(\mathrm{d}^8)$ is a function of a crystal field parameter Δ_{cf} at low pressures, and does not depend on the crystal field parameter at high pressures:

$$U_{eff}(d^8) = \begin{cases} U_0(d^8) - J + \Delta_{cf} & at \quad \Delta_{cf}/J \le 2, \\ U_0(d^8) + J & at \quad \Delta_{cf}/J > 2. \end{cases} \tag{2}$$

where Δ_{cf}=10Dq is the crystal-field parameter, and J is the Hund's exchange energy. Assuming that Δ_{cf} is a linear function of pressure, we conclude that there should be a discontinuity (a kink) in the behavior of the energygap $U_{\mathrm{eff}} - W$, where W is the bandwidth parameter used in the calculation. This kink occurs at $\Delta_{\mathrm{cf}} = 2J$ and is related to the spin-crossover in the d^7 configuration [22, 23]. We do observe such a kink in reflectivity measurements at about 55 GPa (see Fig. 2(c,d)). Assuming that the outlined model is correct, we have calculated $E_{\mathrm{g}}(\mathrm{P})$ using relevant parameters for NiO [39], and experimental values for pressure slopes of Δ_{cf} [27] and W [39]. The best fit to experimental data is given by the following set of parameters [32]:

$$U_0(d^8) = 5.45 \text{ eV}, \quad J = 0.75 \text{ eV}, \quad W_0 = 1.8 \text{ eV} \tag{3}$$

where W_0 is the estimated bandwidth at ambient pressure [39]. The results obtained from Eq. 2 using fitted parameters are in very good agreement with the experimental data [Fig. 2(d)].

A linear extrapolation of the energy gap to zero value gives very high pressure of metallization at about 1 TPa, however, the actual transition occurs at ~240 GPa. Our estimated parameter $\boldsymbol{x} = U_{eff}/W \sim 2$ at transition (~240 GPa) [32] is in a good agreement with the calculations described above [38], taking into account very approximate correspondence of the calculation methods to the NiO lattice and electronic structure.

In summary, the long-sought insulator-metal Mott transition in NiO [8-10] has been experimentally observed at ~ 240 GPa. The transition was preceded by a strong nonlinear decrease in resistance (almost 20-fold) from 130 to 240 GPa. The resistance drops sharply at the transition by about three orders of magnitude, and shows metallic temperature dependence above the transition pressure. We observe a linear decrease of the E_g (bandgap feature) from reflectivity measurements, with a relative pressure slope similar to the relative pressure slope of the thermal activation energy. The activation energy is much less than one half of the E_g, which indicates non-intrinsic conductivity. The temperature dependence of the resistance does not follow the Ahrenius law, similar to the behavior of non-stoihiometric samples at normal pressure. The predictions of the first principles calculations [26] and a simple semiquantitative approach [22-24] imply that metallization should occur at ~1 TPa, However, the observed that the transition to the metallic phase occurs around 240 GPa and is quite sharp. The onset of the insulator-metal transition at 240 GPa is in good agreement with the Mott picture of the IMT which predicts metallization when the effective Mott-Hubbard gap is equal to the full bandwidth $U_{eff} \sim 2W$. Given the fundamental importance of the sample to the understanding of strongly correlated electronic systems, our findings should stimulate further experimental and theoretical studies of NiO, a prototype Mott insulator.

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Figure captions

Figure 1. The images of a NiO sample at 35 GPa **(a)** and 240 GPa **(b)**. The four Pt leads are connected to the NiO sample in the central part of the cBN gasket. At the transition pressure (240 GPa), the NiO sample becomes brown in color (semiconducting phase) and the metallic phase forms black percolation paths in the region ofthe highest pressure between the two electrodes **(b)**. The cBN gasket is nearly transparent at these conditions.

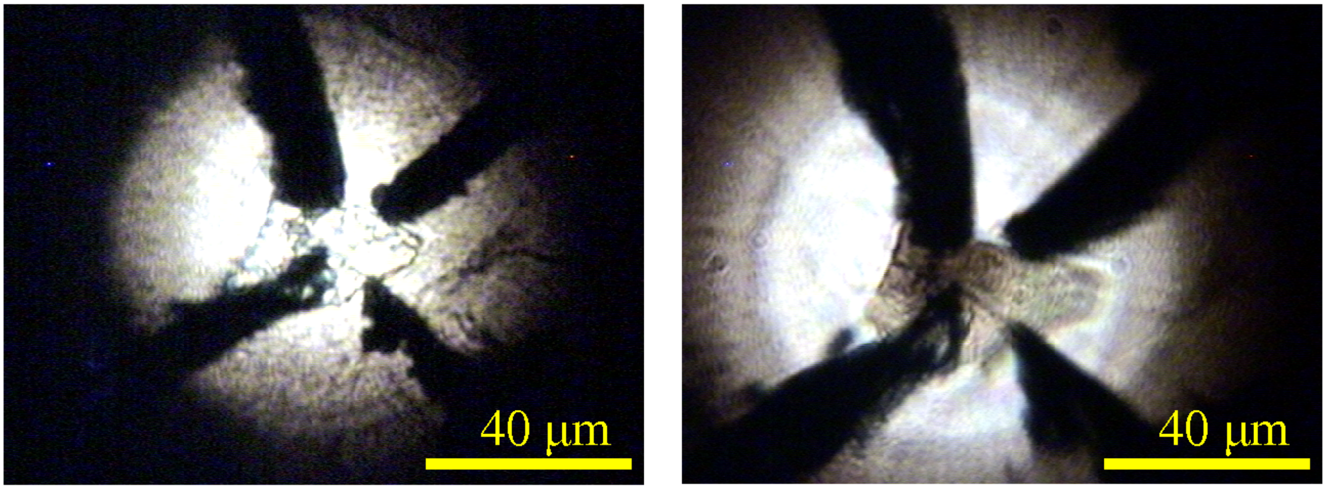
(c) A strong nonlinear decrease of resistance in NiO sample has been measured at room temperature under compression. We observe a sharp drop of resistance into a metallic state (see inset) at the transition pressure P_T = 240±10 GPa. The data from several runs are shown in the inset. The resistance is normalized to the resistance R_T just before the transition.

Figure 2. **(a)** The dependence of $Log_{10}(R)$ on 1/T at several pressures.

(b) The transition from semiconducting to metallic type resistance behavior in NiO at ~240GPa.

(c) The evolution of optical reflectivity spectra of NiO. The spectra are shifted along the vertical, zero reflectivity level is shown by dashed lines. The reflectivity spectrum at ambient pressure (0 GPa) is from the work of Newman and Chrenko (Ref. [36]) .

(d) The pressure behavior of the energy gap E_g in comparison with the behavior of the thermal-activation energy estimated at room temperature. The model calculation [32] of the E_g (using Eq. 2) is shown as solid lines. The pressure dependence of the thermal-activation energy E_{ac} is multiplied by a factor 20 for better comparison. The line drawn through the experimental activation energy points is guide to the eye.



35 GPa
(a)

240 GPa
(b)

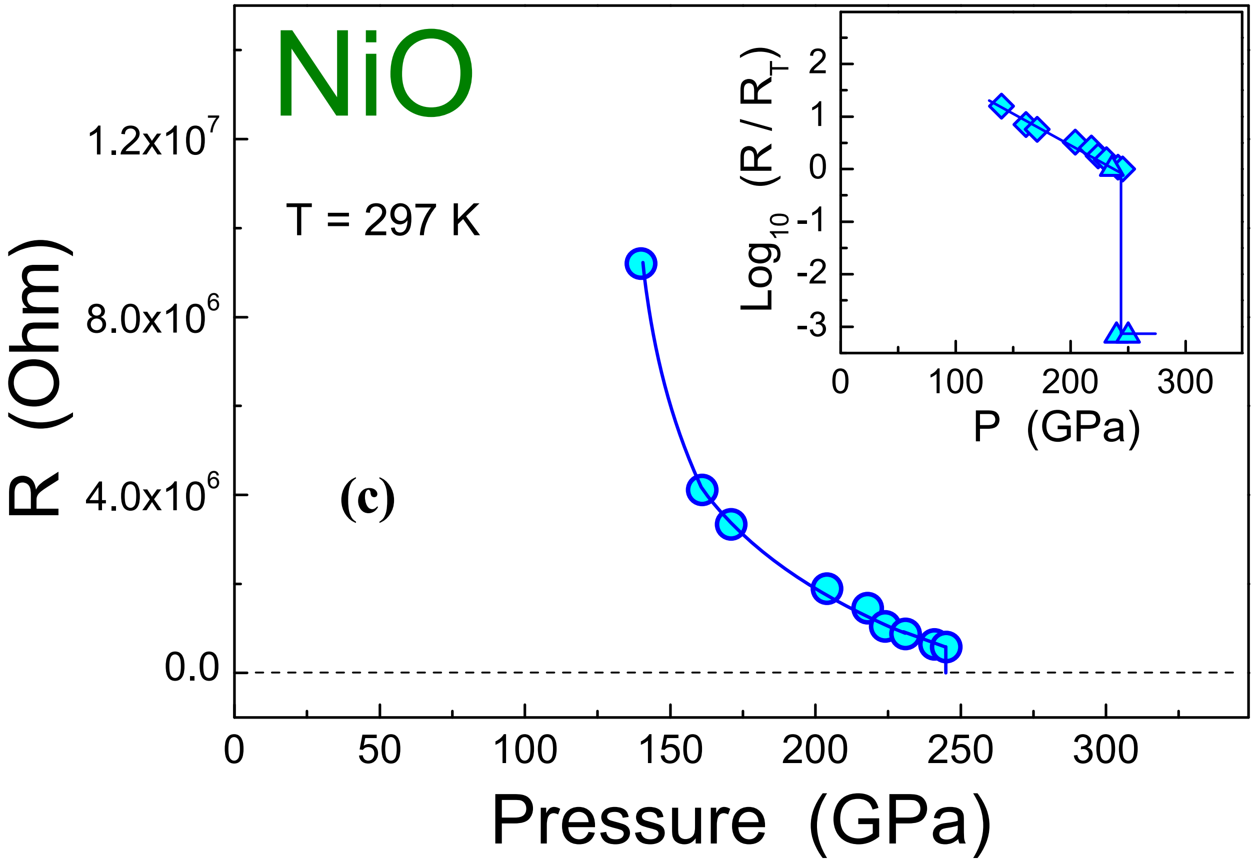


Figure 1.

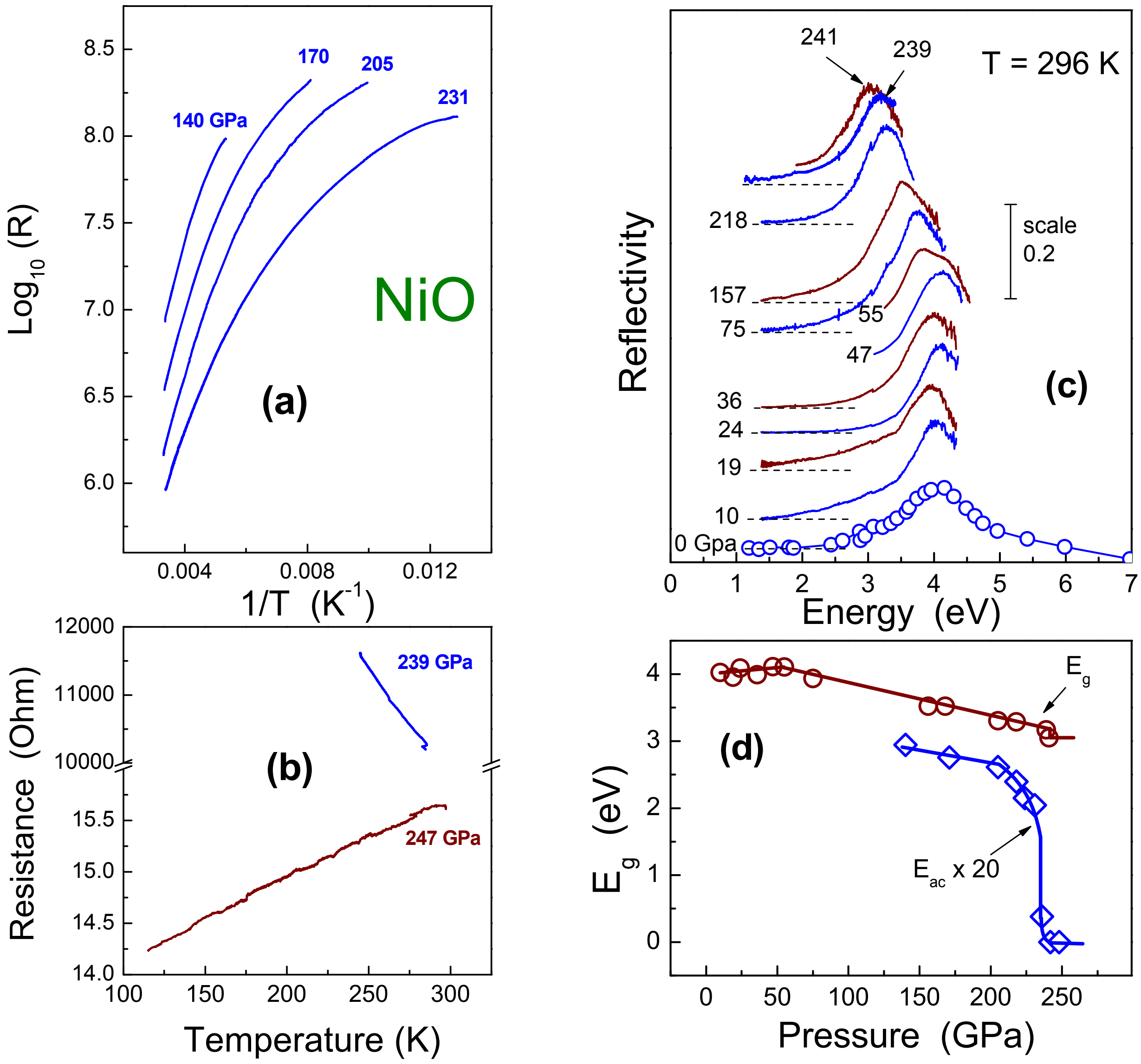

Log_{10} (R)
8.5
8.0
7.5
7.0
6.5
6.0
140 GPa
170
205
231
NiO
(a)
0.004
0.008
0.012
1/T (K^{-1})
Resistance (Ohm)
12000
11000
10000
15.5
15.0
14.5
14.0
239 GPa
(b)
247 GPa
100
150
200
250
300
Temperature (K)
Reflectivity
241
239
T = 296 K
218
scale
0.2
157
55
75
47
(c)
36
24
19
10
0 Gpa
0
1
2
3
4
5
6
7
Energy (eV)
E_g (eV)
4
3
2
1
0
E_g
(d)
E_{ac} x 20
0
50
100
150
200
250
Pressure (GPa)

Figure 2.

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