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Transport phenomena in ammonium halides under high pressures[*]

G.V. TIKHOMIROVA[**], A.N. BABUSHKIN

Physics Department, Ural State University, Lenin Avenue 51, Ekaterinburg, 620083, Russia

Polycrystalline ammonium chloride (NH_4Cl), fluoride (NH_4F) and bromide (NH_4Br) were studied at pressures from 20 to 50 GPa in the temperature range of 77–400 K. Phase transitions from a high-resistance to low-resistance state was found. The transition pressures were about 15 GPa for NH_4Br, 27 GPa for NH_4Cl, and 42 GPa for NH_4F. The transition temperatures and pressures were shown to depend on the preliminary pressure treatment. All ammonium halides show metal-like behaviour under high pressures, similar to that of alkali halides.

Key words: *ammonium halides; high pressure; resistivity*

1. Introduction

Alkali halides of cubic structure with mainly ionic bonds have been studied as model objects for high-pressure physics [1–3]. However, ammonium halides, with the ion $(NH_4)^+$ being an analogue of an alkali metal, have hardly been studied at high pressures at all. Their structures have been studied only up to 9 GPa [4, 5]. In this work, the conductivity of ammonium chloride (NH_4Cl), fluoride (NH_4F), and bromide (NH_4Br) under high uniaxial pressures from 15 to 50 GPa in the temperature range of 77–400 K was studied. Similar to microscopic structural analysis, i.e. X-ray or Raman-scattering measurements, transport measurements can be used to detect phase transitions. Recently, for NH_4Cl and NH_4F, we have found a transition from a high-resistance state to a low-resistance one under high pressures. In this paper, we present studies of this transition in these two ammonium halides and, additionally, in NH_4Br. The time dependence of the resistivity of the ammonium halides with changing pressure was also studied.

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[**] Correspomding author, e-mail: galina.tikhomirova@usu.ru.

2. Experimental

High pressures were generated in a high-pressure cell with synthetic carbonado-type diamond “rounded cone-plane” anvils [6]. These anvils are good conductors and can be used as electric contacts, making it possible to measure temperature and pressure dependencies of resistance. At the temperatures and pressures used, the contact resistance did not exceed several ohms. The behaviour of the samples was examined during several pressure cycles. The samples, produced by a high-pressure treatment from powder materials of chemical purity, were ~0.2 mm in diameter and 10–30 μm in thickness.

3. Results and discussion

A hysteresis in the pressure dependence of resistivity was observed for the ammonium halides studied (Figs. 1, 2). For all three materials, a sharp decrease in resistivity by orders of magnitude from more than 10^8 Ohm to kOhms was observed above some threshold value P_{c2}. On reducing pressure down to $P_{c1}<P_{c2}$, the materials returned to their high-resistive state. P_{c1} was about 42, 25–27 and 15–17 GPa for NH_4F, NH_4Cl

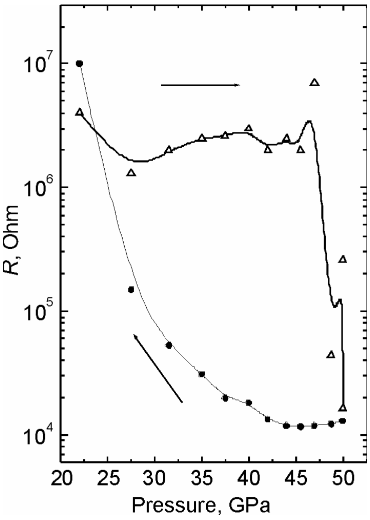

Fig. 1. Pressure dependencies of resistivity of NH_4Cl at room temperature

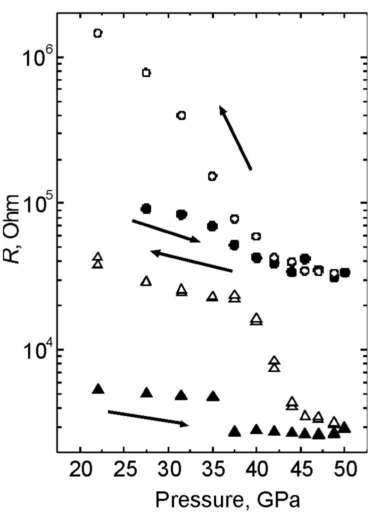

Fig. 2. Pressure dependencies of resistivity of NH_4Br at room temperature: circles – initial increasing and decreasing pressure, triangles – after long exposure under stress

and NH_4Br, respectively. A similar sharp transition was observed near P_c in the temperature dependence of resistivity (Figs. 3, 4). The values of P_c correspond to a stationary state, which was reached after sufficiently long exposure of the samples to stress. The time of pressure treatment necessary to stabilize P_c was quite different for the three materials. Initial loading of the samples with the pressure of 50 GPa caused a change in the resistance only after one-month exposure to stress for for NH_4F, and for about 10 days for NH_4Cl. NH_4Br samples did not require long pressure treatment; they became conductive at P_{c2} = 20–22 GPa. There is a correlation between the times of treatment, as well as the values of P_c, and the densities of the materials (the atomic weight of the halogens F, Cl and Br).

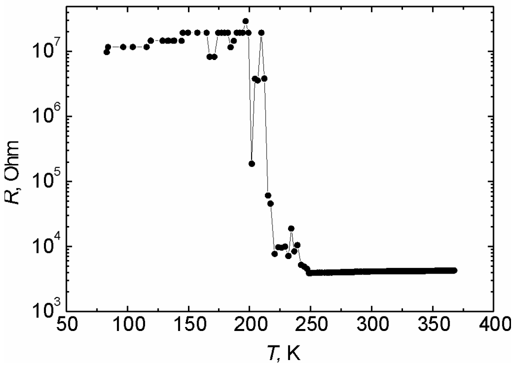

Fig. 3. Temperature dependence of resistivity of NH_4Cl at the pressure $P_{c1} \approx 27$ GPa

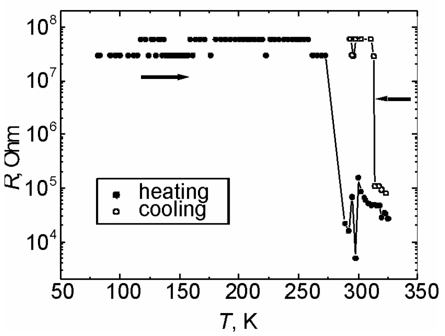

Fig. 4. Temperature dependence of resistivity of NH_4F at the pressure $P_{c2} \approx 50$ GPa

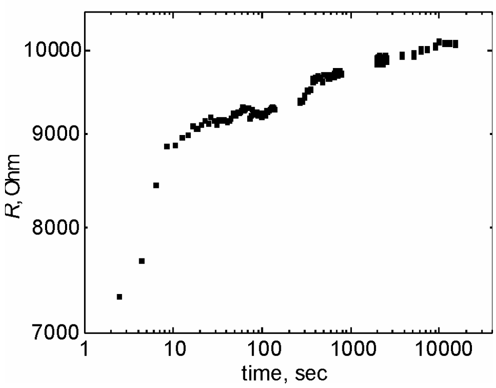

Fig. 5. Time dependence of the resistance of NH_4Br

Relaxation times of conductivity were found to be different for increasing or decreasing pressure (Fig. 5). The time dependencies of resistivity also demonstrated quite different relaxation times: one was seconds; another could be hours or days. The relaxation time was essentially larger at pressures near P_{c1}. At pressures far above P_{c1}, the relaxation times were several minutes. At pressures between P_{c1} and P_{c2}, a thermal hysteresis of the resistance of all three materials was observed, indicating the existence of intermediate states. The magnitude of hysteresis decreased after each cycle of applied and removed pressure and/or after each time of exposure to a high pressure. All ammonium halides have shown a metal-like behaviour under high pressures similar to that of alkali halides. Details of the behaviour of the resistance for each of the ammonium halides are given below.

Ammonium fluoride. The main feature of the temperature dependencies of the conductivity of NH_4F under pressure was hysteresis; it is likely to be due to compacting the polycrystalline structure of the sample by a thermal expansion under high pressure. On heating, the conductivity had a metal-like character up to some critical temperature. The conductivity was practically temperature independent at higher temperatures. A long application of pressure, for several weeks, dramatically changed the character of the temperature dependence as it became metal-like. Below 42 GPa, a reversible transition from a low-resistive state (kOhms) to a high-resistive state (more than 100 MOhm) was observed independently of previous pressure treatment. (For more details, see [8].)

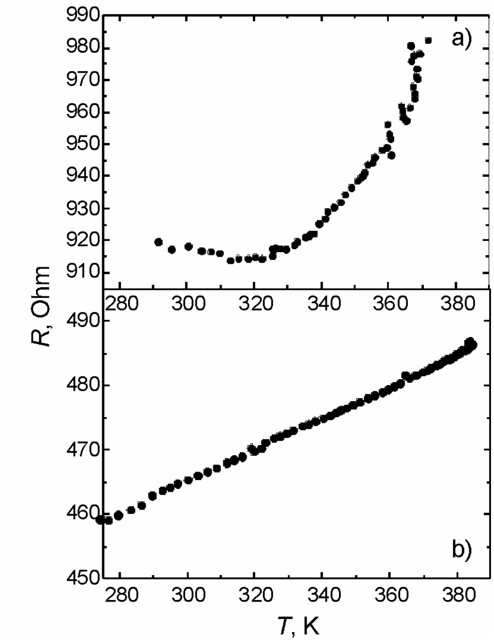

Fig. 6. Temperature dependencies of resistivity of NH_4Cl at 45 GPa: a) after two weeks, b) after two-month exposure under high pressure

Ammonium chloride. The pressure dependence of the resistivity of NH_4Cl was similar to that of NH_4F. However, the temperature dependencies were quite different. The conductivity of NH_4Cl at temperatures below 340 K had an activated character. At temperatures higher than the critical value, a transition to the metal-like state was observed. A minimum in the $R(T)$ dependence indicates the existence of a transition to an intermediate state. This transition did not disappear after long (up to six months) exposure to stress, but was observed in this case only at pressures below 35 GPa.

Figure 6 shows the temperature dependencies of the resistivity of NH_4Cl at 45 GPa after high-pressure treatment for 2 weeks (a) and for more than 2 months (b). Below 25–27 GPa, all ammonium chloride samples became high-resistive (MOhms).

Ammonium bromide. The temperature dependencies of the resistivity of NH_4Br had a positive slope in the temperature range 77 to 300 K. At pressures from 40 to 44 GPa and temperatures above 300 K, anomalies in the dependencies were found, indicating a transition to another state. The transition of ammonium bromide into a high-resistive state was observed at pressures below 15–20 GPa, depending on previous pressure treatment.

4. Conclusion

Phase transitions are shown to exist in ammonium halides at high pressures. They are revealed by sharp changes in resistance by several orders of magnitude. Above the transition, the resistivity is, as a rule, metal-like and similar to that of alkali halides. However, after a period of time, a non-monotonic dependence of resistivity on temperature was observed, indicating the existence of intermediate states. The data obtained show that transport measurements can be used to recognize phase transitions in ammonium halides. To determine the microscopic structure of the phases, X-ray or Raman-scattering measurements are needed.

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