High pressure induced phase transition dynamics in ammonium halides

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Abstract
Comparative studies of high-pressure effect on the resistivity of ammonium halides NH4X (X=F, Cl, Br) at the temperatures of 77 to 400 K are presented. High-pressure phase transitions are found being apparent in a sharp change of the resistance by orders of magnitude at some critical pressures and a hysteresis typical for 1st-order phase transitions. The critical pressure values correlate with the material density being approximately 40, 27 and 15 GPa for NH4F, NH4Cl and NH4Br, respectively. Relaxation times of resistivity at changing pressure are determined. The relaxation of resistivity obeys the exponential law at the pressures far enough from the critical ones; the relaxation times are tenths seconds to minutes. Near the critical pressures, the resistivity relaxation becomes highly non-exponential; the time delay of hours to days appears before the phase transition (the resistance jump).

Introduction
Alkali halides of cubic structure with mainly ionic bonds are well-studied model objects for high-pressure physics [1 to 3]. However, ammonium halides, with the ion (NH4)+ being an analogue of an alkali metal, have not been studied yet at high pressures. The structural investigations of ammonium halides have been only done up to pressure of 9 GPa [4, 5]. We are not aware of any high-pressure transport measurements performed for these materials. Transport measurements under pressure can be used, as well as microscopic structure analysis, i.e. X-ray or Raman-scattering measurements, to detect phase transitions. In this work, comparative studies of resistivity and its relaxation times for polycrystalline ammonium chloride (NH4Cl), fluoride (NH4F), and bromide (NH4Br) under high uniaxial pressures from 15 to 50 GPa in the temperature range 77 to 400 K are presented.

Experimental
High pressures have been generated in the high-pressure cell with synthetic carbonado-type diamond anvils of the "rounded cone-plane" type [6]. The anvils are good conductors and were used as electric contacts making possible to measure temperature and pressure dependences of resistance. At the temperatures and pressures used, the contact resistance did not exceed several Ohms. The method used allows us to study the same sample at successive increasing and decreasing pressure. The estimation of pressure was proved previously at extensive studies of different materials in a wide range of temperatures and pressures [3, 7]. The accuracy of the estimation depends on mechanical properties of the compressed material and is less than 10% in the range of 15 to 50 GPa. The samples, produced by a high-pressure treatment from powder materials of chemical purity, were ~0.2 mm in diameter and 10 to 30 µm in thickness. The voltage across the samples was kept to 10 mV or less to avoid electric breakdown. The measured resistance values were limited by the intrinsic resistance of the measuring circuit, which was around 100 MOhm. Resistivity measurements were carried out in linear part of current-voltage characteristics. The temperature of the high-pressure cell was registered by a copper–Constantan thermocouple.

General features of the resistance of ammonium halides under high pressures
The resistance of all ammonium halides studied exhibited hysteresis as a function of pressure. At low pressures, the resistance of the investigated samples exceeded 10 MOhm. At a certain critical pressure P{sub c2}, the resistance of the ammonium halides studied decreased sharply (with a jump). Subsequent lowering pressure led to the inverse transition to a state with high resistance at a critical pressure P{sub c1} < P{sub c2}. Similar sharp transition was observed in the temperature dependence of resistivity at the pressures close to P{sub c} (Fig.1, 2). The hysteresis in the temperature dependence of the resistance is also observed. The size of the hysteresis loop of the resistance in both pressure and temperature decreases with the...
increase of number of compression–decompression cycles and/or with the increase of time holding samples under pressure tending to a stationary value.

Note that \( P_c \) values mentioned above correspond to a stationary state, which was reached after sufficiently long exposure of samples under stress. The time of pressure treatment necessary to stabilize this jump in resistance is quite different for these three materials. Initial loading samples with pressure of 50 GPa causes the marked change in resistance only after the exposure under stress during a month for \( \text{NH}_4\text{F} \) and about 10 days for \( \text{NH}_4\text{Cl} \). \( \text{NH}_4\text{Br} \) samples don’t require the long pressure treatment; they became conductive at the pressures of 20 to 22 GPa. There exists the correlation between the exposure time, as well as values of \( P_c \), and the density of the materials (the atomic weight of halogens F, Cl and Br).

It was found that the relaxation time of the electrical resistance of the samples after a change in pressure depends on the applied pressure. Near the pressures of the transition from the low-resistance to the high-resistance (> 100 MOhm) state, the relaxation time increases substantially. At pressures \( P > P_{c1} \) (in the region of the conducting phase), both the temperature and pressure dependences of resistance exhibit features indicating the formation of intermediate states. All three ammonium halides at pressures above \( P_{c1} \) (after a preliminary hold under pressure) pass into a state characterized by growth of the resistance with temperature. The details of behavior of the resistance \( R \) for each of three ammonium halides are given below.

**Ammonium fluoride** Fig. 1 shows \( R(T) \) for \( \text{NH}_4\text{F} \) sample at the pressure \( P = 50 \) GPa at heating and cooling. It is seen that for \( 77 \text{ K} < T < 270 \text{ K} \) the resistance exceeds 30 MOhm. As the temperature is increased, the resistance decreases in a jump by at least three orders of magnitude. On subsequent cooling, the sample passes again into the high-resistance state but at somewhat higher temperatures. An additional hold of the sample under pressure of 50 GPa leads to further decrease of \( R \) (to tens of Ohms). The main feature of the temperature dependence of conductivity of \( \text{NH}_4\text{F} \) under pressure is the hysteresis; it is likely due to compacting polycrystalline structure of the sample by a thermal expansion under high pressure. At heating, the conductivity has a metal-like character up to some critical temperature \( T_c \) (from 322 to 335 K for different pressures). The resistivity is practically independent of \( T \) at higher temperatures. The characteristic temperature, at which the temperature dependence of resistivity changes the slope, is practically independent of pressure. A long (several weeks) application of pressure changes dramatically the character of the temperature dependence: it becomes metal-like over entire temperature range studied. Below 42 GPa, a reversible transition from low-resistive state (kOhms) to high-resistive state (more than 100 MOhm) is observed independent of previous treatment by pressure. (For more details, see [8].)

**Ammonium chloride** At the initial application of pressure, samples of \( \text{NH}_4\text{Cl} \) undergo a transition to a state with a resistivity of less than \( 10^3 \) only after a hold of the order of a week.
under the pressure of 50 GPa. In a hold at a lower pressure (44 GPa) the time necessary for transition of the sample to a state of high resistance increases to 17–20 days. The long relaxation time of resistance of NH₄Cl (just as for NH₄F) does not allow us to determine the exact value of the critical pressure Pₑ₂ at which the transition from the high-resistance (above 10⁷) to the conducting state occurs. The return to the high-resistance state at decreasing pressure occurs at Pₑ₁ ≈ 25–27 GPa independently of the prehistory of the sample. At pressures near the critical ones, an analogous sharp (jump-like) transition is observed in the R(T) dependence of NH₄Cl samples (Fig. 2). The jump in resistance by more than three orders of magnitude indicates the presence of a phase transition. The non-monotonocities (jumps) of the resistance near the transition are due to the pressure non-uniformity in the sample and are apparently due to processes of non-uniform compaction (phase fluctuations) of the structure under pressure. Thus, the observed transition of NH₄Cl (like that of NH₄F) from the high-resistance to the low-resistance state upon application of pressure has the characteristic features (the hysteresis, threshold values of pressure, critical fluctuations) typical of a first-order phase transition. The change of the size of the hysteresis loop with the duration of holding samples under pressure is due to the long relaxation times of resistance. In the region of the conducting phase, one observes temperature hysteresis of the resistance that vanishes (as in the case of NH₄F) after a long hold of the sample under pressure. In the first compression–decompression cycles, the temperature dependence of the resistance is of an activation character. After a long (two-month) hold of the samples under pressure, the temperature coefficient of the resistance changes sign. When the pressure is reduced to values close to 27 GPa, the form of the R(T) curves changes noticeably. A common feature of the curves, independent of the duration of preliminary pressure treatment, is a minimum in R(T) at a certain temperature (see Figs. 5 and 6 of Ref. 8). Below that temperature, the temperature has an activation character, while at higher temperatures the temperature coefficient of resistance is positive, i.e., one observes a “semiconductor–metal” transition [9]. The charge carrier density in the state with the positive temperature coefficient of resistance, estimated from measurements of thermopower, does not exceed 10²⁷ m⁻³, which is two orders of magnitude lower than the electron densities in metals. The sign of the thermopower remains unchanged in the region of metal-like conduction and indicates an n-type conductivity.

**Ammonium bromide** For ammonium bromide NH₄Br, unlike the fluoride and chloride, the resistance is not higher than 1–2 MOhm at the pressure P ≈ 15 GPa. In the first cycle, as the pressure is increased from 15 to 30 GPa, the resistance decreases by at least two orders of magnitude. Upon further increase of pressure, the resistance changes only slightly. After a long hold under pressure, the R(P) curve displays a feature at P ≈ 40 GPa, indicating the formation of a new state of the sample. We note that the resistance of NH₄Br is larger at decreasing pressure than at increasing pressure, i.e., the effect is opposite to that observed in NH₄F and NH₄Cl. All the pressure dependences of resistance of NH₄Br characteristically exhibit a decrease in the width of the hysteresis loop for P > 40 GPa and a noticeable increase of R at lower pressures. As to the pressures Pₑ₁ and Pₑ₂ of the transition between the high-resistance and low-resistance states, it is clear that Pₑ₁ lies below the lower limit of our measurements, 15 GPa. The pressure Pₑ₂ could not be determined because of the sharp growth in the relaxation time of the resistance in the pressure interval 15 to 22 GPa. The R(T) curves for NH₄Br have the positive temperature coefficient of resistance at 77 to 300 K. At the pressures of 40–44 GPa, one observes features indicating the transition of the sample to a different state. We note that both the

![Fig. 3. Dependence of the critical pressure on the cation–anion distance.](image-url)
temperature and pressure dependences of resistance of the ammonium bromide differ substantially from those for the other ammonium halides. Similar features have been observed previously for alkali metal bromides, as well [2]. The foregoing results show that all the ammonium halides studied exhibit a phase transition between states with high and low resistance. Figure 3 shows the dependence of the critical pressure $P_{c1}$ on the cation–anion distance $r_{ca}$ at the corresponding pressure. This distance was calculated by means of the universal equation of state by Schlosser, Ferrante, and Vinet [(2.44) in Ref. 10], which gives the dependence of the relative volume $V/V_0$ on $P$. The cation–anion distance $r_{ca}$ is assumed equal to $(V/V_0)^{1/3}$. The dependence $r_{ca}(P_c)$ turns out to be linear, which shows that the transitions in all ammonium halides studied are of the same type.

**Relaxation of the resistance of ammonium halides**

The main difficulty in the measurements of the resistance of ammonium halides as a function of pressure or temperature is the presence of long relaxation times. Unless this circumstance is taken into account the results of measurements can be strongly distorted. Shown in Fig. 4 is the example of such misunderstanding. The temperature dependence of resistance was measured near the transition point. One can see the change of resistance by orders of magnitude. Really, all the change seen is just due to the long relaxation time (being in this case hours to days) comparable with the duration of measurements.

**Fig. 4. Temperature dependence of resistivity of NH$_4$Cl at $P_{c1}$≈27 GPa during transition**

**Fig. 5. Time dependence of relative resistance of NH$_4$Br**

**Fig. 6 Pressure dependence of the relaxation time of resistance of NH$_4$Cl and NH$_4$Br samples after lowering pressure.**
At pressures $P_{c1} < P < P_{c2}$, the relaxation of the resistance of NH$_4$Cl and NH$_4$Br obeys the exponential law of the form (Fig. 5):

$$R(t) = R_s + Ae^{-t/\tau},$$

where $R(t)$ is the resistance at the time $t$, $R_s$ is the steady-state value of resistance, $\tau$ is the characteristic relaxation time, and $A$ is a numerical factor.

Fig. 6 shows the pressure dependence of the relaxation time $\tau$ of the resistance of NH$_4$Cl and NH$_4$Br. It is seen that the relaxation time at pressures near $P_{c1}$ increases noticeably. The $\tau(P)$ curve for ammonium bromide also displays a feature near 40 GPa, which correlates with the features in the pressure and temperature dependences of resistance.

The long-term relaxation of the resistance is especially important near the critical pressures. When the critical pressure is approached, the resistance relaxation becomes essentially non-exponential and non-monotonic (Fig. 7, 8). The relaxation of the resistance near the transition from the high-resistance to the low-resistance state is characterized, as a rule, by two times. Figure 7 shows the dynamics of the change in the resistance of an NH$_4$Br sample in the time following a lowering of the pressure from 27 to 22 GPa. It is seen that the change in resistance occurs with two markedly different times. The short time amounts to a few seconds, while the long time is a number of hours (or even days). The long time can vary depending on the duration of a preliminary hold of the sample under pressure and the value of the applied pressure (on by how much the applied pressure exceeds the critical pressure). At pressures considerably higher than $P_{c1}$, the relaxation time amounts to several minutes.

**Conclusion** All investigated ammonium halides NH$_4$X ($X = F, Cl, Br$) show the transition from high-resistivity to low-resistivity state under high pressure. The transition has characteristic features typical of a first-order phase transition: a sharp (jump-like) change in resistance by several (more than three) orders of magnitude at a threshold pressure, large fluctuations near the transition point and the hysteresis of the resistance in dependence on pressure. The values of the critical pressure correlate with the density of the material (with the cation–anion distance) and are 40, 25–27, and 15 GPa for NH$_4$F, NH$_4$Cl, and NH$_4$Br, respectively. An analogous jump-like transition is observed in the temperature dependence of the resistance at pressures near the critical ones.

The relaxation time of the resistance depends substantially on the pressure: in the pressure region near the transition, the relaxation time increases strongly (from a few hours to days). At pressures significantly higher than $P_{c1}$, it is not more then several minutes.

Like alkali metal halides, all of the ammonium halides studied, when subjected to pressures above $P_{c1}$ and a certain hold under pressure, exhibit a transition to a state characterized by growth of the resistance with temperature.
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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References