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Magnetic Properties of the $Ca_nFe_2Ti_{n-2}O_{3n-1}$ Perovskite Related Series: An EPR Study

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We report here an EPR study of the perovskite-like family $Ca_nFe_2Ti_{n-2}O_{3n-1}$, where Ti^{4+} non-magnetic ions substitute for Fe^{3+} in the brownmillerite structure ($n = 2$). For terms $n = 3$ and 4, intense EPR spectra above ≈ 330 K associated with the resonance of paramagnetic Fe^{3+} ions are observed. The integrated intensity of the EPR line presents a maximum at $T_0 = T(I_{max}) \approx 330$ K in both cases, becoming negligible for $T < 275(5)$ K. Dc magnetic susceptibility measurements present a pronounced break in the slope of χ_{dc} (T) vs T at 283(3) K in both compounds. These anomalies are taken as indications of the establishment of magnetic ordering in the materials. The depression of the ordering temperature found for the terms $n = 3$ and 4 of the series, as compared to the case of $n = 2$, is discussed in terms of the possible cationic order in these compounds. A reduction of the dimensionality of the magnetic behavior is suggested in going from $n = 2$ to $n = 3$ and 4.

I. Introduction

Non-stoichiometry in oxide materials with perovskite (AMO_3) related structures is a topic of current interest in materials science research. The cationic substitution with ions in a different oxidation state allows for the formation of stoichiometric and non-stoichiometric compounds with general formula AMO_{3-y}. The composition range of known compounds varies from AMO_3 to $AMO_{2.5}$, changing from a complete anionic sublattice (perovskite) to one with $\frac{1}{6}$ of unoccupied anionic sites. Frequently, $AMO_{2.5}$ crystallizes in a brownmillerite-type structure (*1*) in which 50% of the cations are surrounded by an octahedral array of oxygen ions as in the perovskite structure. The remaining 50% are surrounded by oxygen ions in tetrahedral coordination. The latter

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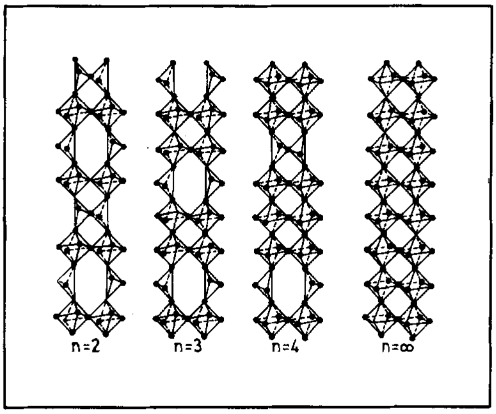

FIG. 1. Structural model corresponding to the members of the $A_nM_nO_{3n-1}$ series, with $n = 2, 3, 4$, and ∞.

sites are arranged in layers intercalated in the perovskite lattice as shown in Fig. 1. Between these two structures, other intermediate phases have been isolated (*2, 3*) with general formula $A_nM_nO_{3n-1}$, where $y = 1/n$ is the number of oxygen vacancies in the perovskite structure. These compounds form according to a structural model in which $(n - 1)$ octahedral planes alternate with a tetrahedral one. In Fig. 1, we show the structure of the compounds reported up to now, which correspond to $n = 2$, $(A_2M_2O_5)$, $n = 3$, $(A_3M_3O_8)$, $n = 4$, $(A_4M_4O_{11})$, and $n = \infty$, (AMO_3).

For M = Fe and $n = 2$, the compound $Ca_2Fe_2O_5$ crystallizes in the brownmillerite structure, which can be described as formed by a sequence of planes . . . OTOT′ . . . , where O corresponds to an octahedral plane and T or T′ to the two possible orientations of the tetrahedra (see Fig. 1). The Fe ions occupy the two different sites forming two sublattices. At variance with other ferrites (*4*), where the Fe^{3+} ions in two different sites give rise to ferrimagnetic order, $Ca_2Fe_2O_5$ is an antiferromagnet (*5*) with a Néel temperature, $T_N = 730$ K. Below T_N, it has been proposed (*5*) that each crystalline layer (octahedral or tetrahedral) orders antiferromagnetically with interplane interactions also of antiferromagnetic nature. The resulting magnetic lattice is similar to that of the Fe^{3+} ions in the perovskite (*6*) $LaFeO_3$, where each magnetic ion is surrounded by six others with opposite magnetic moments.

Grant *et al.* (*7*) and Grenier *et al.* (*8*) have analyzed the behavior of the brownmillerite family of solid solutions $Ca_2Fe_{2-x}M_xO_5$, where part of the Fe^{3+} ions have been replaced by diamagnetic ions, $M = Ga^{3+}$, Al^{3+}, or Sc^{3+}. Their Mössbauer results have shown that (Ga^{3+} or Al^{3+}) and Sc^{3+} substitute preferentially for Fe^{3+} ions in tetrahedral and octahedral sites, respectively, diluting the (T, T′) or the (O) layers. Similar initial rates of depression of T_N were observed in both cases, suggesting that the intra-plane interactions are, on the average, of the same magnitude for the two magnetic sublattices. It has also been speculated in Refs. (*5*) and (*7*) that inter-sublattice interactions may be of the same order of magnitude.

When different cations sharing the M positions in the AMO_{3-x} lattice have mixed oxidation states, the compositional variations may lead to new stoichiometric compounds. This is the case of Ti^{4+} substitution in $Ca_2Fe_2O_5$, where the brownmillerite structure is modified (*2, 3*) through the insertion of additional octahedral planes, forming new materials with general formula $Ca_nFe_2Ti_{n-2}O_{3n-1}$. The stacking sequence of planes is . . . OTOOTO . . . for $n = 3$ and . . . OTOOOT′O . . . for $n = 4$, as shown in Fig. 1. A higher degree of cationic ordering is expected in these compounds (*2*) as compared to the solid solutions with Ga^{3+} and Sc^{3+}, due to the strong preference of Ti^{4+} ions for octahedral coordination and to the difference in oxidation state with respect to Fe^{3+}. It is a problem of interest to analyze in which way this cationic order affects the magnetic behavior of these new materials. We report in this work an electron-paramagnetic resonance (EPR) study of this series of compounds, and we discuss the magnetic ordering temperatures determined from our results, in terms of the possible cationic arrangement within the magnetic lattice.

II. Experimental Results

Polycrystalline samples of $Ca_nFe_2Ti_{n-2}O_{3n-1}$, with $n = 2, 3, 4$, and ∞, were prepared from stoichiometric amounts of $CaCO_3$, α-Fe_2O_3, and TiO_2, following the procedure described in Ref. (*3*). X-ray diffraction analysis of the samples showed single phase materials in all cases, with no indication of impurity phases within experimental resolution. The EPR measurements were performed with a Bruker spectrometer operating at 9.3 GHz in the temperature range between 77 and 650 K. Dc Magnetization measurements were also performed using a Faraday Balance Magnetometer in the temperature range from 60 to 400 K.

As n increases within this series of compounds, a progressive dilution of the magnetic ions, Fe^{3+} ($3d^5$; $^6S_{5/2}$), with the nonmagnetic ions, Ti^{4+} ($3d^0$), is accomplished. For $CaTiO_3$, which corresponds to $n = \infty$, no EPR spectrum was observed, as expected for the case of Ti^{4+} ions alone. $Ca_2Fe_2O_5$, on the other end of the series, shows a weak and complex spectrum in the temperature range of our experiments, which is below the Néel temperature of this magnetic system (*7*), $T_N \approx 730$ K. The field for resonance is temperature dependent and approaches a value corresponding to $g = 2$ for the highest temperature achieved. This could be a spectrum associated with a resonance mode of the ordered phase, shifted from $g = 2$ at low temperatures due to the effect of a temperature-dependent effective magnetic field. However, due to the small intensity of this line and the limited temperature range of our spectrometer (as compared to T_N), no definite conclusions could be drawn with respect to its origin.

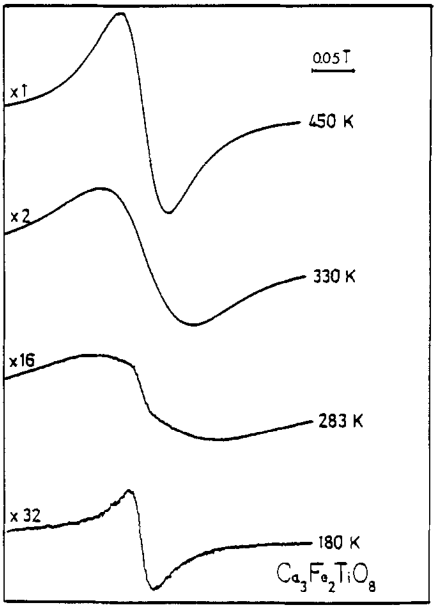

FIG. 2. EPR spectra of $Ca_3Fe_2TiO_8$ taken at different temperatures.

In the case of the compounds $Ca_3Fe_2TiO_8$ and $Ca_4Fe_2Ti_2O_{11}$ (the $n = 3$ and $n = 4$ members of the series, respectively) very intense spectra were observed above ≈ 330 K. These spectra are strongly temperature dependent, as illustrated in Figs. 2 and 3. In the high temperature limit, the lineshape is Lorentzian, with an average peak-to-peak linewidth, $\Delta H_{pp} \approx 0.05$ Tesla for $T > 400$ K. The center field corresponds to a temperature independent gyromagnetic factor $g = 2.00(2)$, as expected for paramagnetic Fe^{3+} free ions. The intensity of the EPR lines, $I(T)$, obtained by numerical double integration over a magnetic field interval much larger than the peak-to-peak linewidth, varies with temperature for both compounds. At high temperatures, where proportionality of $I(T)$ with the paramagnetic susceptibility of the Fe system is expected, the ratio of intensities corresponding to the two compounds is $I_{n=4}/I_{n=3} \approx 0.75$ at 600 K, in good agreement with the relative concentration of Fe ions. Both spectra increase their intensity with decreasing temperature, following

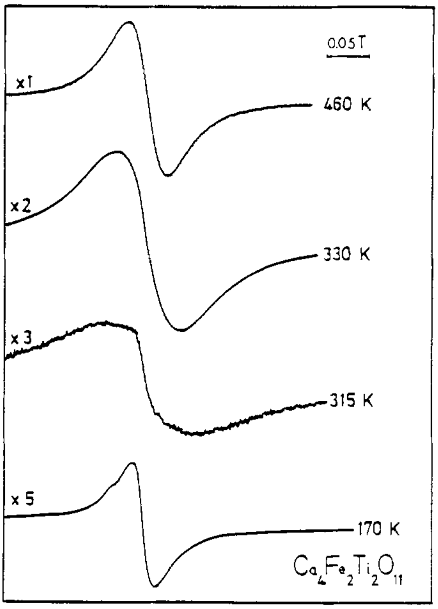

FIG. 3. EPR spectra of $Ca_4Fe_2Ti_2O_{11}$ taken at different temperatures.

approximately a Curie-like dependence, as shown in Fig. 4. The intensity curves present a broad maximum at $T(I_{max}) \approx 330$ K, followed by a fast decrease at lower temperatures. Below ≈ 260 K these EPR lines were no longer detected and a second resonance was observed, although much weaker and centered at an also temperature-independent but slightly higher g-value, $g = 2.01(1)$. This line is also present at higher temperatures, but it is very difficult to separate from the more intense one previously described (see Figs. 2 and 3). The linewidth of the main resonance increases with decreasing temperature, being ΔH_{pp} $(n = 4) < \Delta H_{pp}$ $(n = 3)$ in the whole temperature range measured. This broadening process becomes more pronounced below $T \approx 400$ K as shown in Fig. 5, reaching maximum values of 0.17 Tesla and 0.11 Tesla at $T \approx 280$ K for $n = 3$ and 4, respectively.

The dc magnetic susceptibility, χ_{dc} (T), measured with an applied field of 0.25 Tesla is shown in Fig. 6. It presents a pronounced discontinuity in the derivative, $d\,[\chi(T)]/dT$, at 283(3) K for both $n = 3$ and $n = 4$ compounds. At temperatures higher than ≈ 340 K, the susceptibility follows approximately a Curie–Weiss-like behavior compatible with the nominal content of Fe^{3+} ions in the materials. However, the narrow temperature range of the measurements, as compared with the estimated Curie–Weiss temperature ($\Theta \approx 500$–900 K), prevented an accurate determination of the effective magnetic moment. For temperatures below 283 K, χ_{dc} (T) increases at a much lower rate with decreasing temperature. For $n = 4$ a second break in the κ_{dc} (T) slope vs T was found at $T \approx 170$ K. However, no feature was observed in the already weak EPR spectrum.

III. Discussion

The fact that the EPR spectra have a constant g-factor and the integrated intensity $I(T)$ follows a Curie-like temperature dependence, indicates that the compounds with $n = 3$ and 4 are paramagnetic above $T \approx$

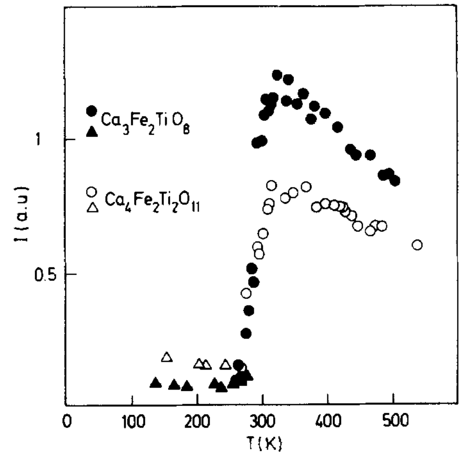

FIG. 4. Double integrated intensity of the EPR line, $I(T)$, measured for $Ca_nFe_2Ti_{n-2}O_{3n-1}$. Full and open symbols correspond to $n = 3$ and 4, respectively. The circles correspond to the main EPR line and the triangles to the weaker line observed at low temperatures.

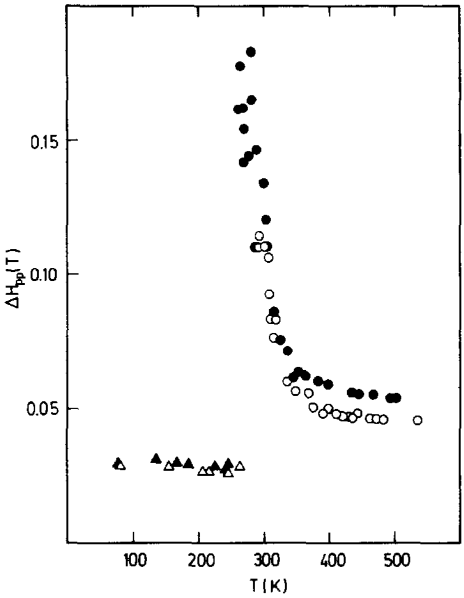

FIG. 5. EPR peak-to-peak linewidth, $\Delta H_{pp}(T)$, measured for $Ca_nFe_2Ti_{n-2}O_{3n-1}$. Full and open symbols correspond to $n = 3$ and 4, respectively. The circles correspond to the main EPR line and the triangles to the weaker line observed at low temperatures.

330 K. The slightly larger value of the EPR linewidth in the high temperature limit for $n = 3$, $\Delta H_{pp}(\infty) \approx 0.055$ Tesla, as compared to $\Delta H_{pp}(\infty) \approx 0.045$ Tesla for $n = 4$, is consistent with the relative concentration of magnetic ions. The rapid increase of the EPR linewidth below ≈ 400 K suggests that the magnetic system approaches a critical temperature (*9*). Thus, the strong decrease of the integrated intensity observed between 330 and 270 K may be associated with the onset of magnetic order in these materials, which does not allow the paramagnetic resonance mode to be excited. The ordering process is similar for the two compounds, and the maximum of the integrated EPR intensity defines a characteristic temperature $T_0 = T(I_{max}) \approx 330$ K in both cases. This temperature is coincident with the observed deviation of $\chi_{dc}(T)$ from the high temperature Curie–Weiss behavior.

The observed temperature dependence is similar to that found (*8*) for different solid solutions $Ca_2Fe_{2-x}M_xO_5$, where the Fe magnetic lattice of $Ca_2Fe_2O_5$ was magnetically diluted through M = Al, Sc, and Ga substitutions. Comparison with the Néel temperatures determined in Ref. (*7*) from Mössbauer effect measurements indicates a close coincidence with the temperatures at which the magnetic susceptibility presents the break in slope. Thus, we have associated by analogy the slope break at $T_N = 283(3)$ K with the ordering temperature of the $Ca_nFe_2Ti_{n-2}O_{3n-1}$ compounds, with $n = 3$ and 4.

A comparison may be made with $Ca_2Fe_{2-x}M_xO_5$, when M is the non-magnetic ion Ga^{3+} or Sc^{3+}. In that case, T_N decreases monotonically with increasing dilution and the rate of depression is similar for both ions (*7*). This occurs in spite of the fact that Ga^{3+} and Sc^{3+} tend to preferentially (although not exclusively) substitute for Fe^{3+} ions in tetrahedral and octahedral sites, respectively. For dilutions nominally equivalent to those in our compounds with $n = 3$ and 4, the interpolated values for the Néel temperature are $T_N \approx 490$ K ($x = 0.67$) and $T_N \approx 315$ K ($x = 1.00$), respectively.

For Ti^{4+} substitution, instead, we have found a different pattern for the dependence of the ordering temperature on magnetic dilution. T_N (and even T_0) is much lower for $n = 3$ than the corresponding T_N for Ga^{3+}, Al^{3+}, or Sc^{3+} substitution. On the other hand, it remains unchanged at $T_N \approx 283(3)$ K with further dilution to $n = 4$. As it has been pointed out in Ref. (*8*), the cationic distribution in the dilute magnetic lattices strongly affects the mean number of magnetic neighbors for a given concentration of non-magnetic ions. Thus, it is an important variable that controls the dependence of the ordering temperatures on the Fe concentration. The rather different behavior that we have found for Ti substitution may well be related to a large degree of cationic order

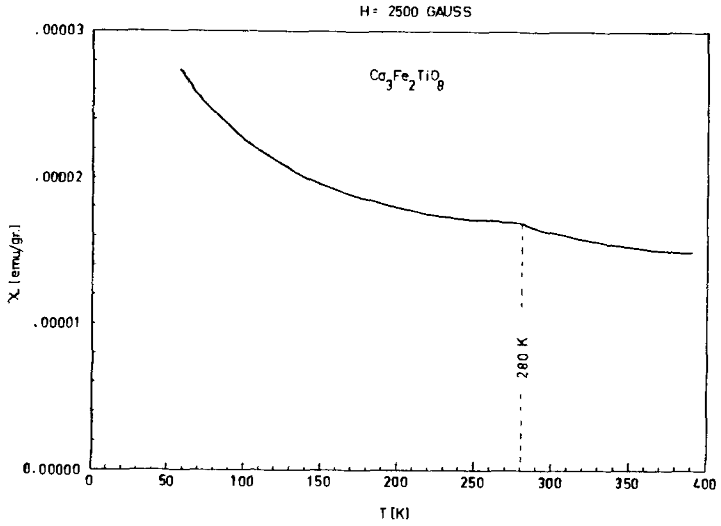

FIG. 6. Dc magnetic susceptibility for $Ca_3Fe_2TiO_8$, measured with an applied magnetic field of 0.25 Tesla. The arrow indicates the break in slope associated with the magnetic ordering of the lattice.

present in the compounds, since there are evidences (*10*) that in other cases of heterovalent substitution, the ions with different valence tend to occupy ordered sites in the crystal structure. Although it has not been possible to experimentally detect cationic order in our compounds from X-ray powder diffraction data (*3*) due to the similarity of the scattering factors of Fe and Ti ions, it has been proposed (*3*) that at least partial order may exist, based on the strong preference of Ti^{4+} ions for octahedral coordination. Thus, the tetrahedral layers may be occupied almost exclusively by Fe^{3+} ions, although the octahedral ones may contain either Fe^{3+} or Ti^{4+} ions.

In this case the magnetic structure would preserve, when diluted with non-magnetic Ti^{4+} ions, layers of tetrahedrally coordinated Fe^{3+} ions with almost no Ti^{4+} substitution. These T (or T') layers are strongly coupled in $Ca_2Fe_2O_5$ through the octahedral sites, forming a three dimensional magnetic system. For $n = 3$ (or 4) the tetrahedral planes are separated by a layer consisting of two (or three) perovskite (O) planes, where the magnetic dilution is believed to take place preferentially. The average Fe concentration in these layers would then be 50 and 33%, respectively. For $n = 3$, there are some structural similarities with the case of $Ca_2Fe_{1.5}Sc_{0.5}O_5$, where there are also tetrahedral planes almost fully occupied (97%) by Fe^{3+} ions (*7*) and separated by single octahedral layers with an average Fe^{3+} concentration of 50%. However, the thicker perovskite layer (two unit cells) in the Ti compound seems to reduce the effective coupling between the T planes and thus the ordering temperature. An even weaker coupling might be expected for $n = 4$ due to the larger separation (three unit cells) between (T) planes and the lower concentration (33%) of magnetic ions in the intermediate layer, but no further reduction of T_N was observed. Based on these observations, we suggest that the observed behavior may be mainly related to magnetic ordering of the tetrahedral lattice. If this interpretation were correct, a change of the magnetic dimensionality of the magnetic lattice might occur in going from $n = 2$ to $n = 4$. So far, we have considered only cationic order in the tetrahedral planes due to the preference of Ti^{4+} ions for octahedral sites. It should be also taken into account the possibility of cationic order within the perovskite layers, which may have important effects on the strength of interplane coupling. Unfortunately, the available X-ray diffraction studies (*3*) do not allow a determination of the degree of order within these layers.

As previously mentioned, exchange interactions of the same order of magnitude are expected for all nearest magnetic neighbors (*7*), and an estimation of its magnitude may be obtained from the Néel temperature of $Ca_2Fe_2O_5$. An approximate ratio $k_BT_c/J \approx 25$ has been found (*11*) for other compounds where magnetic moments with $S = 5/2$ and similar coordination present 3D magnetic order. Using the average value $J/k_B \approx 30$ K determined in this way, we estimate a ratio $k_BT_c/J \approx 11$ for both $Ca_3Fe_2TiO_8$ and $Ca_4Fe_2Ti_2O_{11}$. This value is significantly lower than the ratios $k_BT_c/J \sim 17$ and $k_BT_c/J \sim 13$ expected for the nominal magnetic dilution of these compounds in a mean field approximation. A comparison with the ratios $k_BT_c/J \sim 18$ and $k_BT_c/J \sim 11$ found (*11, 12*) for 2D square and 1D linear lattices, respectively, suggests that the magnetic ordering evidenced by the EPR experiments is closer to that of 1D systems. This observation is consistent, within the hypothesis of cationic ordering with preferential occupancy of the tetrahedral sites by Fe ions, with the fact that each Fe ion in these sites has only two other Fe ions in the same lattice with Fe–O–Fe bonds favorable to superexchange interactions (*5*).

In conclusion, cationic order in the series $Ca_nFe_2Ti_{n-2}O_{3n-1}$ and subsequent reduction in the magnetic dimensionality expected for the members with $n = 3$ and 4 may explain the dependence of the ordering temperature with magnetic dilution, as determined from EPR and dc magnetization measurements. It may also explain the similarities of the EPR spectra observed for both compounds in the whole temperature range of our measurements. The less pronounced maximum of the EPR intensity found for $n = 4$ may also be attributed to a more clearly defined lower dimensionality of the magnetic lattice.

Finally, we address the weak EPR line observed below T_N. Its temperature-independent g-factor, its slowly increasing intensity for decreasing temperatures, and the additional Curie-like contribution to the magnetic susceptibility found in the same temperature range suggest that the origin of this resonance may be related to small amounts of paramagnetic Fe^{3+} ions in a different environment, decoupled (or only weakly coupled) to the ordered lattice. Since no spurious phase was found in the X-rays diffraction analysis, we may speculate that the observed resonance may arise from paramagnetic ions diluted in extended defects of the crystal structure. In this context the presence of stacking faults corresponding to the intercalation of plane sequences . . . OOO . . . characteristic of the perovskite structure has been reported in Ref. (*3*). Since these defects have been found more often for $n = 4$ than for $n = 3$ compounds, this assignment may explain the relatively more intense low temperature resonance found for $n = 4$. However, a systematic study of the correlation between EPR intensity and density of stacking faults would be needed in order to verify this hypothesis. Also further work is necessary in order to understand the temperature dependence of $\chi_{dc}(T)$ below T_N (including the feature at $T^* \approx 170$ K for $n = 4$).

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