The Al^{27} Knight shift and magnetic properties of Fe, Co, and Ni monoaluminides

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The Knight shifts of Al^{27} and the magnetic susceptibility are investigated in the (78−1100)°K temperature range for $Fe_{0.48}Al_{0.52}$, $Fe_{0.50}Al_{0.50}$, $Fe_{0.51}Al_{0.49}$, $Ni_{0.50}Al_{0.50}$, and $Co_{0.50}Al_{0.50}$ alloys with a CsCl structure. It is shown that the temperature dependence of the magnetic susceptibility and of the Knight shift of Al^{27} in Fe-Al alloys is characteristic of antiferromagnets. Possible causes of the appearance of antiferromagnetism in these alloys are presented. The Al^{27} Knight shift is small in CoAl and NiAl; it is positive and independent of temperature. With respect to magnetic properties these monoaluminides are weak, temperature-dependent paramagnets.

We present here the results of investigations of the Al^{27} Knight shift and magnetic susceptibility in ordered binary alloys of aluminum with iron, cobalt and nickel. It is known from the literature that the magnetic properties and the NMR in the Fe–Al alloys are governed by different mechanisms. NMR and the magnetic susceptibility are attributed in[1] to indirect exchange via conduction electrons and in[2] to the presence in FeAl of a conduction band with high density of p-states at the Fermi level, and to s–d hybridization. The existence of antiferromagnetism in FeAl is also postulated in[3].

The existence of such different opinions is due, first of all, to an insufficient amount of experimental data. In connection with this, we have measured the Knight shift K on Al^{27} nuclei and the magnetic susceptibility χ in a wide temperature range 77–1100°K in the alloys $Fe_{0.51}Al_{0.49}$, $Fe_{0.50}Al_{0.50}$, $Fe_{0.48}Al_{0.52}$, and in the monoaluminides CoAl and NiAl. The monoaluminides FeAl, CoAl, and NiAl have a body-centered cubic structure of the CsCl type, in which the atoms of the transition metal (Fe, Co, Ni) are in the center of the cube, and the aluminum atoms are on the vertices of the cube. In the alloys of the Fe–Al system, with the aluminum concentration less than 50%, some of the aluminum atoms that are on the vertices of the cube are replaced by iron atoms, and in alloys in which the aluminum concentration is 50–52% the aluminum atoms are replacing the iron atoms that are located at the center[4]. The method of preparation of samples used in this work and the results of chemical and x-ray structure analyses are given in[5-7].

The measurements were performed on samples with the mean linear dimensions of the particles of 50 μ, 100 μ, and 1 mm. The samples in the powder form were annealed for 30 min at 750°C. The absorption NMR spectra were recorded with a broad-line NMR spectrometer. The Al^{27} Knight shift was measured relative to the Al^{27} resonance in $AlCl_3$ in magnetic fields of 5–10 kOe. The error in the Knight shift determination was not higher than 0.01% at low temperatures and 0.02% at high temperatures.

The magnetic susceptibility was measured with a pendulum balance, and the error in the magnetic susceptibility was not higher than 3%.

The results of measurements of the magnetic susceptibility of FeAl alloys shows that the susceptibility is strongly dependent on the particle size. Samples with particles of 50 and 100 μ were strong paramagnets with a susceptibility that satisfies the Curie-Weiss law. The susceptibility in the samples with 1-mm particles was two orders of magnitude lower. We should mention that further increase in particle size had no effect on the magnetic susceptibility.

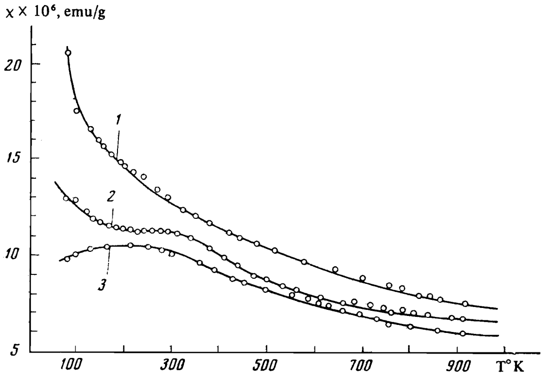

FIG. 1. χ as a function of T for the FeAl samples: 1–51% Fe + 49% Al, 2–50% Fe + 50% Al, 3–48% Fe + 52% Al.

Figure 1 shows the temperature dependence of the specific magnetic susceptibility of the alloys $Fe_{0.51}Al_{0.49}$, $Fe_{0.50}Al_{0.50}$, and $Fe_{0.48}Al_{0.52}$ ($d \sim 1$ mm). From this figure it is apparent that the magnetic susceptibility of $Fe_{0.51}Al_{0.49}$ obeys the Curie-Weiss law, while the susceptibility of the equiatomic compound $Fe_{0.50}Al_{0.50}$ in the 150–350°K range is almost temperature-independent. At lower and higher temperatures the susceptibility χ of this sample depends on T. The magnetic susceptibility of $Fe_{0.48}Al_{0.52}$ increases from 77 to 200°K, and decreases above 400°K. We would like to point out that such a temperature-dependence of the magnetic susceptibility is typical of antiferromagnets[8].

In all the samples, the Al^{27} Knight shift was independent of the size of the particles in the samples and had the same value for all the investigated alloys (Fig. 2). It can also be seen from Fig. 2 that the Al^{27} Knight shift is negative and increases from −0.31% at 77°K to −0.38% at 200°K, it is then constant up to 500°K, and after that it decreases again with further increase of temperature.

The NMR and magnetic-susceptibility measurements of the compounds CoAl and NiAl have shown that the magnetic susceptibility of these compounds is dependent on the size of the particles in the samples and increases with decreasing size. The samples with particle linear

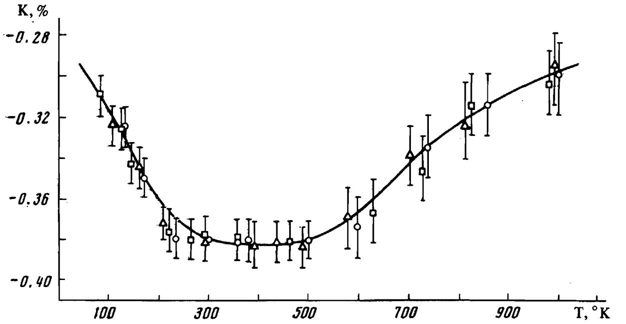

FIG. 2. K as a function of T for the FeAl samples: □—48% Fe + 52% Al, ○—50% Fe + 50% Al, △—51% Fe + 49% Al.

dimensions 1 mm and larger are weak paramagnets, the susceptibility of which is almost temperature-independent. The magnetic susceptibility of NiAl is equal to $\sim 15 \times 10^{-6}$ emu/mole, and that of CoAl is $\sim 30 \times 10^{-6}$ emu/mole.

The Knight shifts of Al^{27} and Co^{59} are also temperature-independent and have small positive values for the aluminum nuclei, 0.05% for NiAl and 0.01% for CoAl, and 0.6% for the cobalt nuclei in the compound CoAl. A gyromagnetic ratio $\gamma/2\pi = 1005.3$ Hz/G was used for the determination of the Co^{59} Knight shift.

No correlation can be detected between the temperature dependences of the Knight shift of Al^{27} nuclei and of the magnetic susceptibility of the equiatomic $Fe_{0.50}Al_{0.50}$. From this lack of correlation it can be assumed that the local magnetic moments at the Fe atoms in the Al sites are responsible for the increase of susceptibility in the low-temperature region.

Indeed, according to[9], there is no possibility of obtaining complete ordering in the monoaluminide FeAl, because there is always a definite number of iron atoms in the Al sublattice. According to theory given in[10], these iron atoms give rise to local moments that introduce a large temperature-dependent component in the magnetic susceptibility. These local moments should have no influence on the behavior of the Knight shift, because the NMR line at the Al atoms near the iron atoms with the local moment broadens and becomes unobservable, and we see only the line from the ordered structure.

This assumption is corroborated by the behavior of K and χ in the alloys $Fe_{0.51}Al_{0.49}$ and $Fe_{0.48}Al_{0.52}$. Indeed, addition of some surplus of iron to the monoaluminoid increases the number of iron atoms on aluminum sites[4]. This should bring, according to our assumption, an increase in susceptibility, as is indeed observed in the alloy $Fe_{0.51}Al_{0.49}$. To the contrary, addition of some surplus Al to FeAl decreases the probability of finding an iron atom on the aluminum site, and the local moments should disappear, as is observed in the alloy $Fe_{0.48}Al_{0.52}$. As to the Al^{27} Knight shift, there should be no change in its behavior, as is indeed experimentally confirmed. We note also that it follows from the temperature dependences of the Knight shift and the susceptibility in $Fe_{0.48}Al_{0.52}$ that there is a correlation between these quantities.

As is known, the Knight shift on nuclei of a non-transition metal in a compound with a transition metal is given by[11]

$$K=K_0-\beta\chi_d, \qquad (1)$$

where K_0 is the temperature-independent contribution due to conduction s-electrons, β is a constant coefficient, and χ_d is the spin-susceptibility of d-electrons. From the temperature dependence of the Knight shift and Eq. (1) it follows that with increasing temperature the spin susceptibility should at first increase and then decrease, as is indeed observed in experiment (see Fig. 1, curve 3). The presence of local moments in the other investigated alloys makes the magnetic susceptibility of the ordered structure of $Fe_{0.50}Al_{0.50}$ difficult to observe, and in this case no correlation was observed between the Knight shift and the magnetic susceptibility.

From the NMR and the magnetic-susceptibility experimental results it follows that in the ordered structure $Fe_{0.50}Al_{0.50}$ there is, most likely, an antiferromagnetic ordering with a very broad peak.

Antiferromagnetic ordering in a sublattice of iron ions occupying their sites can be attributed to the existence of negative interatomic exchange interaction in the sublattice of iron ions, as suggested by E. I. Kondorskiĭ in his explanation of the anomaly in Invar alloys[12]. We are not excluding the possibility of the occurrence of a standing spin wave in the d-band[13], the stability of which is aided by the high density of electronic states on the Fermi level[14], which was experimentally determined in[15], and found to be three times larger than in pure iron.

We note that in the compounds NiAl and CoAl, which have the structure of FeAl, a low density of electronic states on the Fermi level was observed[16]. This seems to be the reason why their magnetic and resonance properties differ from those of FeAl.

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