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Antiferromagnetic Structure of $AlCr_2$†

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Body-centered tetragonal $AlCr_2$ has been shown by neutron diffraction to be antiferromagnetic below the Néel temperature of 598°±5°K. The spin structure obtained from the neutron powder data is characterized by an antiferromagnetic coupling between the adjacent Cr layers in the *c*-layer sequence, Al–Cr↑–Cr↓–Al–, where each Cr layer forms a ferromagnetic sheet. The magnetic moment of Cr is 0.92±0.02 Bohr magneton and the moment inclines 65±2° from the *c* axis. Neither crystal nor magnetic transition was observed below 598°K down to 1.6°K. The Debye temperature of $AlCr_2$, 472±8°K, was obtained from the coherent nuclear-scattering data.

INTRODUCTION

THE compound $AlCr_2$ was selected for the neutron diffraction study, since its crystal structure[1] belongs to the CaC_2-type structure that has been one of our major subjects.[2] However, in $AlCr_2$ the Cr–Cr bonds forming a staggered *c* layer are much stronger than a weak Cr–Cr bond that would otherwise assume a Cr_2 group similar to a C_2 group in CaC_2. In this aspect, the crystal structure of $AlCr_2$ is closely analogous to $MnAu_2$ whose magnetic spin structure[3] has demonstrated one of the first examples of the spiral-spin alignment. However, as regards the magnetic atom, $AlCr_2$ and $MnAu_2$ are antisomorphic to each other. Although the magnetic susceptibility of $AlCr_2$ is hitherto unknown, the interatomic distances suggest probable magnetic-spin ordering of Cr in $AlCr_2$. As described below, we have found that this is indeed the case and this paper describes the nature of the spin coupling in $AlCr_2$. Besides $AlCr_2$ and $MnAu_2$, no other aligned-spin structure of the CaC_2-type compound has been studied. All of the statistical errors in the following sections are expressed in terms of the standard deviation.

CRYSTALLOGRAPHIC DATA

The sample was prepared by slow cooling of the stoichiometric melt. As found by Bradley and Lu,[1,4] this process gives an inhomogeneous mixture consisting of $AlCr_2$ with a tetragonal structure (β) and a small amount of the Al–Cr solid solution having a body-centered cubic structure (α). In fact, our ingot contains scattered large-grained high-luster fragments which are easily distinguishable from the greyish, fine-grained main body. The former gave the α-structure x-ray pattern, while the latter x-ray pattern showed only the β structure. The ingot product is brittle. Hence, separation of the two constituents and the crash-grinding powder preparation were readily performed. The β-$AlCr_2$ samples, about 10 μ in average particle size, were then sieved out for the neutron studies.

A spectroscopic analysis of our neutron sample revealed the significant metallic impurities, 0.06 wt % of Fe and 0.1% of W. The chemical analysis showed Al 79.6±0.2% and Cr 20.2±0.1%, indicating a slightly Cr-deficient composition[4] (the theoretical values, Al 79.40% and Cr 20.60%). The x-ray diffraction study gave the body-centered tetragonal lattice constants at 298°C,

$$a=3.006\pm0.002\text{ A}, \qquad c=8.663\pm0.005\text{ Å},$$

and

$$c/a=2.882,$$

while Bradley and Lu[1] have obtained

$$a=3.00446\text{ A}, \qquad c=8.64773\text{ Å},$$

and

$$c/a=2.8783.$$

Discrepancy in the *c* lattice constants is due probably to a small difference in the composition. The space group is $D_{4h}^{17}-I_m^4mm$ with two chemical formulas per unit cell. The density and the unit cell volume of our sample are hence 5.554 g/cm³ and 78.28 Å³, respectively. The atomic coordinates are (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$) for Al and (000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$)±(00*z*) for Cr. Our x-ray diffraction data agree with the Cr parameter $z=0.319$ obtained by Bradley and Lu.[1]

NEUTRON DIFFRACTION STUDY

The neutron diffraction patterns of the powdered β-$AlCr_2$ were obtained with $\lambda=1.0683$ and 1.462 Å using an automatic neutron diffractometer and its low- and high-temperature attachments.[5] The total cross section of our sample at 293°K was measured with 1.0683-Å neutrons (0.0717 eV) using the technique described elsewhere.[5] The cross-section value, 13.5±0.2 b, is in good agreement with the calculated value using the atomic cross sections for β-$AlCr_2$.

† Based on work performed under the auspices of the U. S. Atomic Energy Commission.
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[3] A. Herpin, P. Meriel, and J. Villain, Compt. Rend. (Paris) **249,** 1334 (1959).
[4] A. J. Bradley and S. S. Lu, J. Inst. Met. **60,** 319 (1937).
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TABLE I. Observed and calculated intensities for β-$AlCr_2$ at 4.2°K. The calculated value is equal to $F^2\times$(Lorenz factor for $\lambda=1.0683$ Å)$\times$ (temperature factor with $2B=0.279$ Å^2)$\times$(multiplicity factor) in 10^{-24} cm^2, where F is the scattering amplitude for the unit cell. The magnetic reflections are designated by subscript m to the indices.

Indices	I_{calc}		I_{obs}
$(001)_m$	34.6		35.0±0.5
002	2.8		3.9±0.7
$(100)_m$	18.4		18.8±0.5
$(003)_m$	10.4	11.8	11.1±0.5
101	1.4		
$(102)_m$	8.5		8.0±0.9
004	3.7		
110	143.2		
103	261.9	412.7	420±6
$(111)_m$	1.6		
112	2.3		
$(104)_m$	0.1		
$(005)_m$	0.9	4.6	4.3±0.3
$(113)_m$	3.6		
114	7.4		
200	73.0	87.8	86±2
105	7.1		
$(201)_m$	0.3		
006	27.7	29.0	29.2±0.7
202	1.3		
$(210)_m$	0.7		
$(115)_m$	0.6		
$(203)_m$	0.7	3.7	<4
211	0.6		
$(106)_m$	0.6		
$(212)_m$	0.5		

Indices	I_{calc}		I_{obs}
$(007)_m$	0.0		
204	5.0	269.6	272±5
213	187.1		
116	77.5		
107	14.3		
$(214)_m$	0.0	14.5	10±5
$(205)_m$	0.2		
008	1.8		
$(117)_m$	0.0		
220	38.3		
215	7.4		
$(221)_m$	0.0		
206	60.4	109.2	109±3
222	0.7		
$(108)_m$	0.2		
$(300)_m$	0.1		
$(223)_m$	0.1		
301	0.2		
$(216)_m$	0.2		
$(302)_m$	0.1		
118	5.8		
$(009)_m$	0.0		
$(207)_m$	0.0		
224	3.2		
310	63.0		
303	59.6	189.6	189±4
$(311)_m$	0.0		
312	1.2		
109	37.2		
217	19.1		
$(304)_m$	0.0		
$(225)_m$	0.1		
$(313)_m$	0.1		

The diffraction patterns were taken at about a dozen different temperatures between 1.6°K and 900°C. The diffraction curve at 4.2°K is shown in Fig. 1, where all of the extra coherent peaks could be indexed on the chemical unit cell with the condition $h+k+l=2n+1$. The intensities of these extra reflections did not vary noticeably in the temperature region from 1.6°K to room temperature. At above room temperature, the intensities of these peaks decrease appreciably with increasing temperature and the peaks disappear completely above 325°C. The coherent nuclear-scattering reflections following the condition $h+k+l=2n$ remain unchanged up to about 850°C, except for the small effects due to the thermal vibration and expansion. Above 850°C, the crystal structure transforms to the α structure. In addition to the x-ray study, careful analyses were made on the neutron data in order to see whether any of these weak extra peaks in our β-$AlCr_2$ pattern originated from other Al–Cr alloys or the Cr metal. All of these possibilities were discarded. Also, the finely powdered sample exhibits a weak parasitic ferromagnetism. It was then assumed that the extra reflections are magnetic in origin.

The coherent nuclear intensities at high scattering angles were analyzed using the coherent nuclear-scattering amplitudes of 0.35 and 0.352 in 10^{-12} cm for Al and Cr, respectively.[6] The agreement between the observed and calculated intensities in Table I sub-

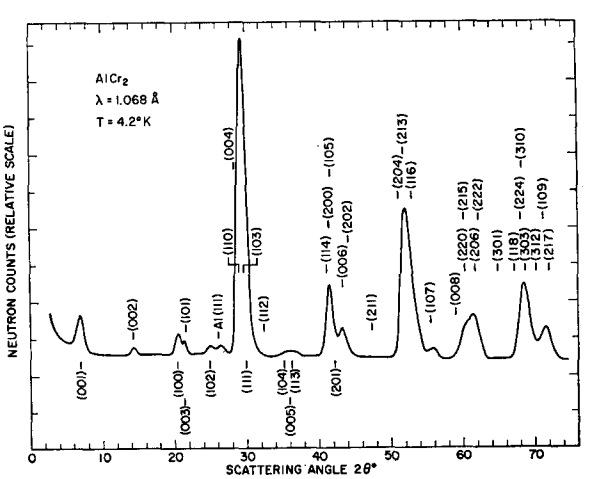

FIG. 1. Diffraction pattern of $AlCr_2$ at 4.2°K. The indices of the antiferromagnetic reflections are given in the background region and those higher than (201) are omitted.

[6] G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, England, 1962); 2nd ed., p. 275.

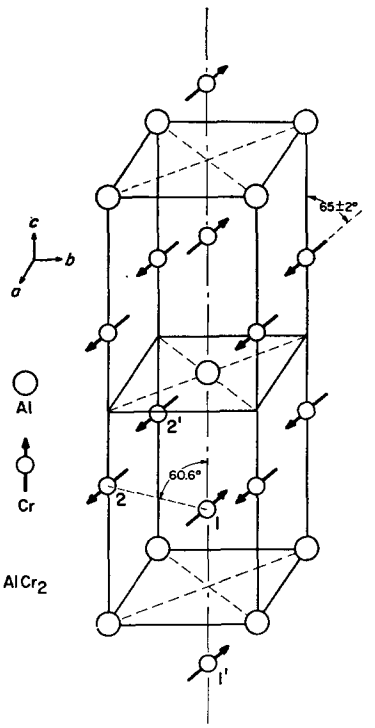

FIG. 2. The unit cell of $AlCr_2$ showing the antiferromagnetic arrangement of the magnetic moments of the Cr atoms.

stantiates the Cr positional parameter described before. As shown in Table I, a number of nuclear reflections possess very weak intensity, and this made the peak analysis considerably easier. The Debye–Waller temperature factor led to the Debye characteristic temperature of 472°±8°K which lies interestingly between the Debye temperatures of Al and Cr, 428° and 630°K, respectively.[7] The temperature variation of the Debye temperature is smaller than ±8°K.

The extra reflections could be explained by assuming an antiferromagnetic structure which is depicted in Fig. 2. This spin structure may be described as Al–Cr↑–Cr↓–Al–Cr↓–Cr↑– in the body-centering *c*-layer sequence. Each Cr layer forms a ferromagnetic sheet. Along the *c* axis, all Cr atoms are ferromagnetically aligned. The inclination of the moment with respect to the *c* axis was found to be 65°±2.4°. This value is insignificantly different from 60.6°, the inclination angle of the Cr1–Cr2 bond relative to the *c* axis (see Fig. 2). Because of the powder data, no information was obtained as regards the spin direction relative to the *a* axis nor possible multispin axis structure. Careful search for a satellitic reflection was in vain and hence the spiral-spin alignment such as observed in $MnAu_2$ is not plausible in $AlCr_2$. The present uniaxial spin structure led to the Cr moment of 0.92± 0.02 Bohr magneton. The magnetic form factor employed is that determined experimentally for Mn^{2+}.[8,9] The magnetic intensity data at 4.2°K are compiled in Table I. Here, the over-all discrepancy factor $\sum | I_{obs} - I_{calc} | / \sum I_{obs}$, inclusive of the nuclear reflections, is as small as 1.3%.

The temperature-dependence plot of the magnetic intensities gave the Néel temperature $T_N = 598° \pm 5°K$. The square of the antiferromagnetic (001) amplitude normalized to that near $T = 0°K$ is shown as a function of T/T_N in Fig. 3. A small correction for the temperature factor has been applied to the observed amplitude. Although each experimental point in Fig. 3 is a statistical average of at least three independent measurements, the weak intensity of the magnetic reflection resulted in a relatively large statistical error. Nevertheless, it may be concluded that the observed data is closely approximated by the Brillouin function with $S = \frac{1}{2}$ which is practically identical to the BCS function.[10,11]

We now discuss briefly the bond nature in $AlCr_2$ utilizing Pauling's bond number[12] which gives a good estimate of the bond strength. The interatomic distance for Cr1–Cr1′ (Fig. 2) is 3.133 Å for which the bond number is only 0.056. Here, the single-bond metallic radius of Cr is taken as 1.191 Å obtained from a precision lattice constant of Cr.[13] The bond number for Cr1–Cr2 is 0.799 (2.440 Å). Thus, as mentioned before, the Cr–Cr bonds forming a staggered *c* layer

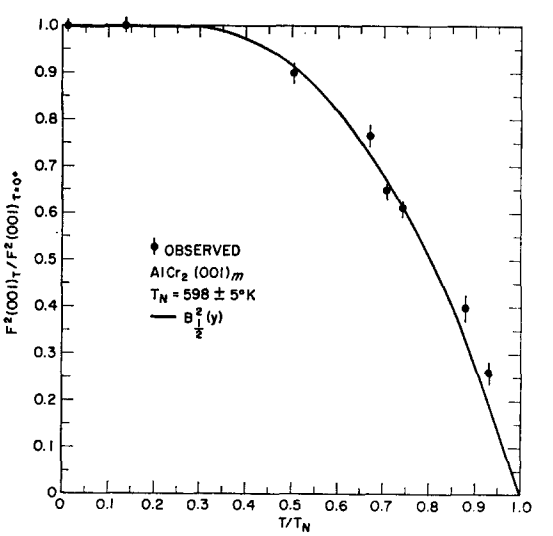

FIG. 3. Variation with temperature of the observed antiferromagnetic (001) intensity of $AlCr_2$. A short vertical line on the experimental point is roughly equal to the standard deviation.

[7] *American Institute of Physics Handbook*, edited by D. W. Gray *et al.* (McGraw-Hill Book Company, Inc., New York, 1963), 2nd ed., Chap. 4., p. 61.

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composed of the tetragonal pyramids are by far stronger than the Cr1–Cr1′ bond. The inclination angle of the Cr moment, which is almost equal to that of the strongest Cr–Cr bond, seems to suggest that the exchange coupling within the Cr double layer could be dominant in determining the spin alignment in $AlCr_2$. The $AlCr_2$ structure may be considered as partial replacement of Cr in the Cr metal by Al. It is of interest to note that both the magnetic moment and the Néel temperature of the Cr metal[14] are about half of the respective values for $AlCr_2$. The antiferromagnetic exchange field[15] in $AlCr_2$ is hence about equal to that in the Cr metal, although the spin structures are quite different in these two antiferromagnets. The bond number for the nearest Cr–Cr approach in the Cr metal is 0.640 (2.499 Å) which is noticeably smaller than Cr1–Cr2 in $AlCr_2$. The neutron study of other Cr-rich Al alloys is in progress so as to obtain further data on the subject.

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Systematic Perturbations of the EPR Spectra of Anthracene and Azulene Anions in Solution* †

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(Received 1 February 1965)

Experimental measurements of the hyperfine coupling constants of anthracene and azulene anions with various solvents and cations are presented. It is shown that the proton coupling constants depend on solvent, cation, concentration, and temperature and that variations of these constants of about 10% can occur. The variation of the proton coupling constants is shown to be systematic and is ascribed to the electrostatic perturbation of the cation. Calculations are presented to support this view. Most of the systems studied are classified as ion pairs, free anions, or equilibrium mixtures on the basis of qualitative features of their EPR spectra. The absence of hyperfine coupling from the counterion does not necessarily indicate that the anion is unassociated.

INTRODUCTION

SINCE de Boer and Weissman[1] studied the EPR hyperfine structure of a number of aromatic ion radicals, many spectra of such radicals have been examined. The hyperfine coupling constants have usually been considered to be characteristic of the radicals involved and have been compared with theoretical predictions for the isolated radicals. Thus, in the study of sodium naphthalene ion pairs in various solvents, Atherton and Weissman[2] found no variation in the proton coupling constants within the experimental accuracy of 3% although the sodium coupling constant did vary. Since then several examples of solvent or counterion dependent coupling constants have been reported for quinones,[3] benzophenone,[4,5] and nitroaromatics.[6,7] A theoretical discussion of solvent effects has been given by Gendell, Freed, and Fraenkel.[8] A few examples of variable coupling constants in hydrocarbons have also been reported, e.g., pyracene,[9] anthracene,[10] and azulene.[11]

A number of studies[12–14] of the optical spectra of the anthracene ion have shown line shifts depending on the alkali ion present. From these, it was concluded that ion pairs were present. It was somewhat puzzling, however, that the EPR spectra showed no metal coupling such as was found[2] with sodium and naphthalene.

In the present paper it is shown that when the proton coupling constants of anthracene and azulene anions are measured with sufficient precision they depend upon

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